

**ABANT İZZET BAYSAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES**



**COMPOSITION AND SOURCE APPORTIONMENT OF
ATMOSPHERIC PARTICULATE MATTER: BOLU CASE**

DOCTOR OF PHILOSOPHY

HATİCE KARADENİZ

BOLU, AUGUST 2017

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DEPARTMENT OF CHEMISTRY



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DECLARATION

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Hatice KARADENİZ

ABSTRACT

COMPOSITION AND SOURCE APPORTIONMENT OF ATMOSPHERIC PARTICULATE MATTER: BOLU CASE

PHD THESIS

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**ABANT İZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES**

DEPARTMENT OF CHEMISTRY

(SUPERVISOR: PROF. DR. SERPİL YENİSOY KARAKAŞ)

BOLU, AUGUST 2017

Totally 326 PM_{2.5-10} teflon filter, 312 PM_{2.5} teflon filter, 172 PM₁₀ quartz filter and 166 PM_{2.5} quartz filter samples were collected in the campus of Abant İzzet Baysal University between March 2013 and February 2014. Teflon filters were used to determine the amounts of anions (F⁻, Cl⁻, NO₂⁻, NO₃⁻, Br⁻, SO₄²⁻) and cations (Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) and elements (Li, Be, Na, K, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Hg, Pt, Au, Pb, Bi, Tl, Th, U). Quartz filters were used to evaluate organic carbon (OC), elemental carbon (EC) and total carbon (TC) in PM₁₀ and PM_{2.5} mode. For the analysis, ICP-MS, ion chromatography and thermal/optical transmittance carbon analyzer were used. The measured concentrations of each parameter were evaluated statistically, seasonally and temporally. Calcium, Al, Fe, Na, Mg, and K had the highest arithmetic mean concentrations. The crustal elements were mostly found in the coarse fraction and the anthropogenic ones were in the fine fraction. The arithmetic means and standard deviations of the particulate matter concentrations were lower in the nonheating season. Particulate matter concentrations were greater than the limit values regulated by law number 4856 of the Ministry of Environment and Forestry in some sampling days. The NO₃⁻/SO₄²⁻ ratio indicated that the sampling site was affected from the coal burning rather than emissions from mobile sources. As a result of cation to anion ratio and multiple linear regression, it was found out that the particulate matter was acidic. The correlations between OC and EC were performed monthly. The high correlation coefficients indicated that they were emitted from the similar sources. The concentrations of primary OC were generally greater than the concentrations of secondary OC. The concentrations of both however showed the increasing trend in the heating season. The source apportionment studies were done by using enrichment factor calculation, wind sector analysis, back trajectories and positive matrix factorization (PMF). The anthropogenic elements were highly enriched in both fractions. The dominant wind sector in the sampling area was from West South West sector. There are no local sources from that direction therefore the long-range transportation is the main

pollution source. The other pollution sources for the anthropogenic elements that were found from the pollution roses were the city center and highways. The results of PMF combined with back trajectories gave 8 factors affecting the sampling site for both particulate modes. They were named as: Traffic, coal and wood burning, aged aerosol, agricultural activities, polluted soil, iron-steel works, soil, sea-long range transportation for coarse particulate matter. The sources for fine particulate matter were as follows: Soil (Saharan effect), urban factor, sea-long range transportation, poultry sector, coal and biomass burning, traffic-mining, aged aerosol, waste incineration-iron-steel works.



KEYWORDS: Coarse PM, Fine PM, Elements, Ions, EC/OC, Source apportionment, PMF

ÖZET

**ATMOSFERİK PARTİKÜL MADDENİN KOMPOZİSYONU VE
KAYNAK PAYLAŞIMI: BOLU ÖRNEĞİ
DOKTORA TEZİ
HATİCE KARADENİZ
ABANT İZZET BAYSAL ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ
KİMYA ANABİLİM DALI
(TEZ DANIŞMANI: PROF. DR. SERPİL YENİSOY KARAKAŞ)**

BOLU, AĞUSTOS- 2017

Abant İzzet Baysal Üniversitesi kampüsünde Mart 2013 - Şubat 2014 tarihleri arasında toplam 326 PM_{2.5-10} teflon filtre, 312 PM_{2.5} teflon filtre, 172 PM₁₀ kuvars filtre ve 166 PM_{2.5} kuvars filtre örnekleri toplanmıştır. Teflon filtreler anyon(F⁻, Cl⁻, NO₂⁻, NO₃⁻, Br⁻, SO₄²⁻) ve katyon (Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) ve elementlerin (Li, Be, Na, K, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Hg, Pt, Au, Pb, Bi, Tl, Th, U) miktarlarını belirlemek için kullanılmıştır. Kuvars filtreler PM₁₀ ve PM_{2.5} modlardaki organik karbonu (OK), elemental karbonu (EK) ve toplam karbonu (TK) değerlendirmek için kullanılmıştır. Analizler için ICP-MS, İyon Kromatografi ve termal/optik transmitans karbon analizörü kullanılmıştır. Her bir parametrenin ölçülen konsantrasyonları, istatistiksel mevsimsel ve zamansal olarak değerlendirilmiştir. Kalsiyum, Al, Fe, Na, Mg ve K en fazla aritmetik ortalamalara sahiptirler. Toprak kaynaklı elementler en çok kaba fraksiyonda bulunurken, insan kaynaklı elementler en çok ince fraksiyonda bulunmuşlardır. Partikül madde aritmetik ortalama konsantrasyonları ve standart sapmaları ısınma olmayan sezonda daha az olarak bulunmuşlardır. Partikül madde konsantrasyonu, bazı örnekleme günlerinde 4856 sayılı Çevre ve Orman Bakanlığının kanunu tarafından belirlenen sınır değerlerden daha yüksek bulunmuştur. NO₃/SO₄²⁻ oranları örnekleme alanının, hareketli emisyonlardan çok kömür yanmasından etkilendiğini göstermiştir. Katyonun anyona oranı ve çoklu lineer regrasyon sonucundan, partikül maddenin asidik olduğu bulunmuştur. OK ve EK arasındaki korelasyonlar aylık olarak yapılmıştır. Yüksek korelasyon katsayıları benzer kaynaklardan atıldıklarını göstermektedir. Birincil OK'nin konsantrasyonları genelde ikincil OK'nin konsantrasyonlarından daha fazladır. OK ve EK'nin konsantrasyonları ısınma sezonunda artan bir eğilim göstermektedir. Kaynak paylaşımı çalışmaları, zenginleşme faktörü hesaplamaları, rüzgar sektörü analizi, geri trajektörler ve pozitif matriks faktörleme (PMF) kullanılarak yapılmıştır. Her iki fraksiyonda da insan kaynaklı elementler çok fazla zenginleşmiştir. Örnekleme alanındaki dominant rüzgar sektörü batı güney batıdır. Bu yönden lokal kaynaklar olmadığından, uzun mesafe taşınım ana kirlilik kaynağıdır. Kirlilik güllerinden bulunan insan kaynaklı kirlleticiler için diğer kirlilik kaynakları şehir merkezi ve otobanlardır. Her iki partikül modunda da geri trajektörlerle birleştirilmiş PMF sonuçları örnekleme alanını etkileyen 8 faktör vermiştir. Kaba partiküller için bunlar trafik, kömür ve odun yanması, yaşlı aerosol, tarımsal aktiviteler, kirlili toprak, demir-çelik işleri, toprak, deniz-uzun mesafe taşınımıdır. Toprak (Sahra etkisi), şehir

faktörü, deniz-uzun mesafe taşınım, kümes hayvanları sektörü, kömür ve biyokütle yakımı, trafik-madencilik, yaşlı aerosol, atık yakımı-demir çelik işleri ince partiküldeki kaynaklardır.



ANAHTAR KELİMELEER: Kaba PM, İnce PM, Elementler, İyonlar, EK/OK, Kaynak paylaşımı, PMF

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LIST OF ABBREVIATIONS AND SYMBOLS

EC	: Elemental carbon
EC_{measured}	: Measured elemental carbon
OC	: Organic carbon
OC_{comb}	: Combustion organic carbon
OC_{measured}	: Measured organic carbon
OC_{non-comb}	: Non combustion organic carbon
OC_{pri}	: Primary organic carbon
OC_{sec}	: Secondary organic carbon
PM	: Particulate Matter
PM_{2.5-10}	: Coarse particulate matter
PM_{2.5}	: Fine particulate matter
USEPA	: United States Environmental Protection Agency

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1. INTRODUCTION

Environmental science is the science of the complex interactions that occur among the terrestrial, atmospheric, aquatic, living, and anthropological environments. It includes all the disciplines, such as chemistry, biology, ecology, sociology, and government that affect or describe these interactions. For example, environmental chemistry studies the sources, reactions, transports, effects, and fates of chemical species in water, soil, air and living environments, and the effects of technology and so on. The importance of the environmental chemistry comes from the determination of pollutants. This is the first vital step in environmental science (Manahan, 2000).

Pollutant is defined as a substance which presents in greater amount in environment because of the human activity and has detrimental effect on human health and environment. However, contaminants are not classified as pollutants until there is a proof about some detrimental effect. Their concentrations are greater than normal composition in environment. Every pollutant or contaminant has been emitted from a source. The source can be natural or anthropogenic. When a pollutant is emitted from a source, it can affect a receptor. The receptor is anything (a person, an animal, a tree, a plant, or a material) that is affected by the pollutant. If the pollutant is resistant in environment, it may be deposited in a sink which is a reservoir. This reservoir deposits a chemical element or compound from another part of environmental cycle (Manahan, 2000; Vallero, 2008).

Human being lives on earth and earth is surrounded by a gaseous layer as a blanket: Atmosphere. Atmosphere protects the earth from outer space. It is the source of carbon dioxide for plant photosynthesis and oxygen for respiration. It also absorbs harmful ultraviolet radiation from the sun and stabilizes Earth's temperature. Unfortunately, there is an increase of human population and these increases affect the environment, especially the atmosphere. For example, the synthesis of organic compounds has grown day by day. Unfortunately, there are limited mechanisms to metabolize and eliminate these new compounds. In addition, with the industrial revolution pollutants have been emitted into the atmosphere and human kind began to face high concentrations of toxic pollutants and interested in improving the quality of entire air sheds (Vallero, 2008). For this manner, atmospheric science, a branch of

environmental chemistry, emerged and helps to deal with the movement of air masses in the atmosphere, atmospheric heat balance, and atmospheric chemical composition and atmospheric reactions. Before studying atmospheric science, it should be known what atmosphere is and why it is important for human.

1.1 Air and the atmosphere

Atmosphere is separated into layers based on temperature. The troposphere is the region in which we live. Therefore, atmospheric pollution is generally studied in this layer. Theoretically, the precise composition of unpolluted air can not be known. Because people have been polluting the air for ages and scientists have realized the importance of determining the atmospheric composition since the nineteenth century. Therefore, the concentration of air is described as diluted polluted air like the most remote location at sea, at the poles and the deserts and mountains (Vallero, 2008). The defined unpolluted air which we live contains approximately 78.1% nitrogen (by volume), 21.0% oxygen, 0.9% argon and 0.03% carbon dioxide, a large variety of trace level gases at levels below 0.002% including neon, helium, methane, krypton, nitrous oxide, hydrogen, xenon, sulfur dioxide, ozone, nitrogen dioxide, ammonia, and carbon monoxide, except water. It also contains 1-3% water vapor by volume (Manahan, 2000).

1.2 Air pollution

As mentioned before, over the past decade, with the growing technology and the human activities, air pollution has been a great problem for humans and environment. Therefore, developed countries produced some solutions for the problem. The general definition of air pollution is

‘The presence of contaminants or pollutant substances in the air that interfere with the human health or welfare, or produce other harmful environmental effects (Vallero, 2008).’

This definition helps thinking about what an air pollutant is. Over the past decades, air pollutants were associated with harm to humans, such as respiratory diseases. Then, this association changed and environmental damage property was also concerned. Clean air act was addressed six air pollutants in 1970. These are

1. Particulate matter (PM)
2. Ozone
3. Carbon monoxide
4. Sulfur dioxide
5. Nitrogen dioxide
6. Lead

and are called 'criteria air pollutants'. Then USEPA regulates two sets of standards. Primary standards are used protecting human health, secondary standards aim to prevent environment (Vallero, 2008).

1.3 Particulate matter

Particulate matter makes up to the most visible form of the air pollution. (Vallero, 2008). Particulate air pollutants consist of materials in solid or liquid phase suspended in the atmosphere. Such particles affect human health (Pope et al., 2009), visibility (Bäumer et al., 2008), air quality and climate change (IPCC, 2007).

Figure 1.1. shows these prototypical size distributions of tropospheric particles with selected sources and pathways of how the particles are formed (Vallero, 2008). According to the figure, if particles which are sufficiently small and have low mass, they can be suspended in the air for a long time. However, particles with diameters greater than 10 μm rarely travel long distances. Therefore, they are generally of less concern and measured if the emitting sources are very close to the sink. Here, the source is the place from which pollutants emitted and sink is the place to which

pollutants disappear from the air. In this transportation, person or animal that breathes the air can be affected from the emitted pollutant (Vallero, 2008).

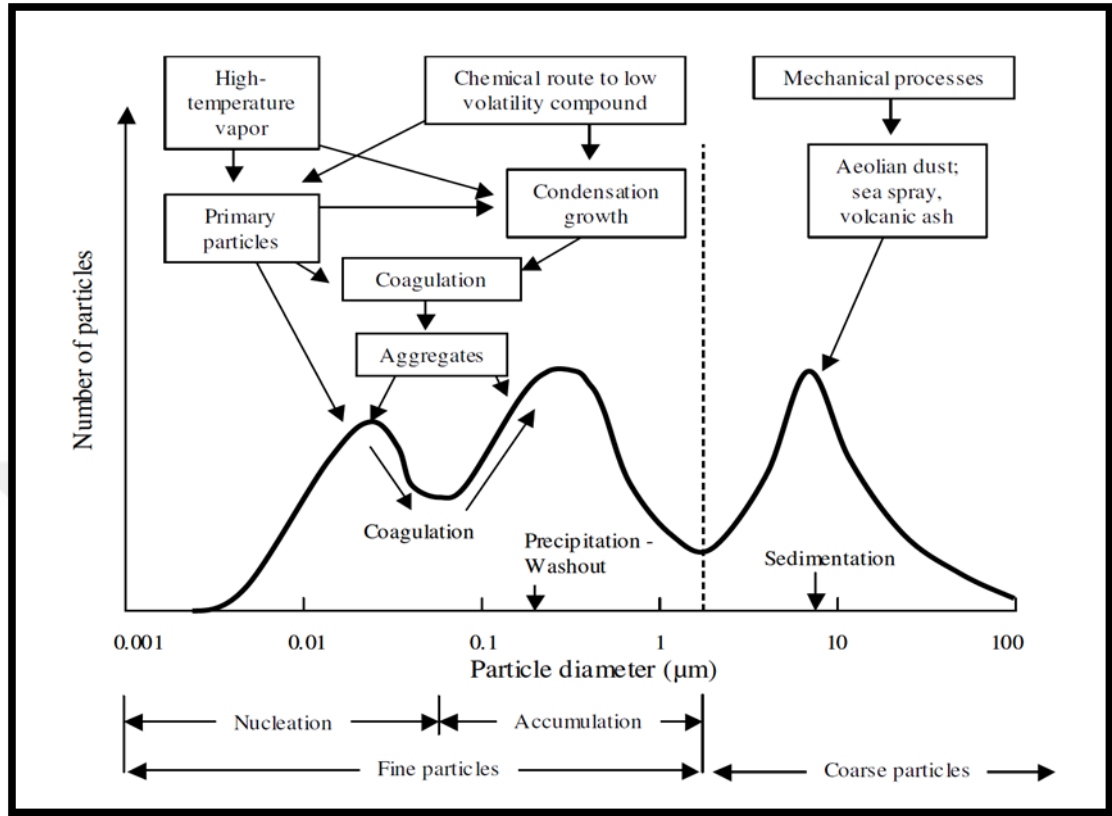


Figure 1.1. The prototypical size distribution of tropospheric particles with selected sources and pathways of how the particles are formed (Vallero, 2008).

Particles have different shapes. However, they are generally assumed to be spherical. Because it is impossible to compute the diameter for unspherical particles. (Heinsohn and Kabel, 1999). The aerodynamic diameter is defined as the diameter of a sphere with standard density that settles at the same terminal velocity as the particle of interest (DeCarlo et al., 2012)

Pollutant particles are suspended in the air near the sources of pollution. Their sizes are between the 0.001 to 10 μm range (Heinsohn and Kabel, 1999) and atmospheric properties are determined by their physical properties which has a strong relationship with size. Generally, two types of particulate matter are measured below 2.5 μm diameter and 2.5 $\mu\text{m} \geq$ and $\leq 10\mu\text{m}$ diameter. Particulate matter which has 2.5 μm diameter is called as fine particles whereas particulate matter which has a diameter between 2.5 $\mu\text{m} \geq$ and $\leq 10\mu\text{m}$ diameter is called as coarse particles (Vallero, 2008).

Coarse particles can be produced by mechanical grinding, windblown dust, sea spray, non-exhaust vehicle emissions, agriculture, construction, and quarrying activities (Charron and Harrison, 2005). They contain the most visible form of PM such as black smoke, soil, dust, salt particles, pollen, mould, spores and other plant parts. On the other hand, fine particles contain primary combustion particles and secondary particles, which produced by coagulation and condensation processes. Some examples of relationship between the size and the composition for particulate matter are shown in Figure 1.2. Particulate matter can be categorized by using chemical identity (organic or inorganic pollutants).

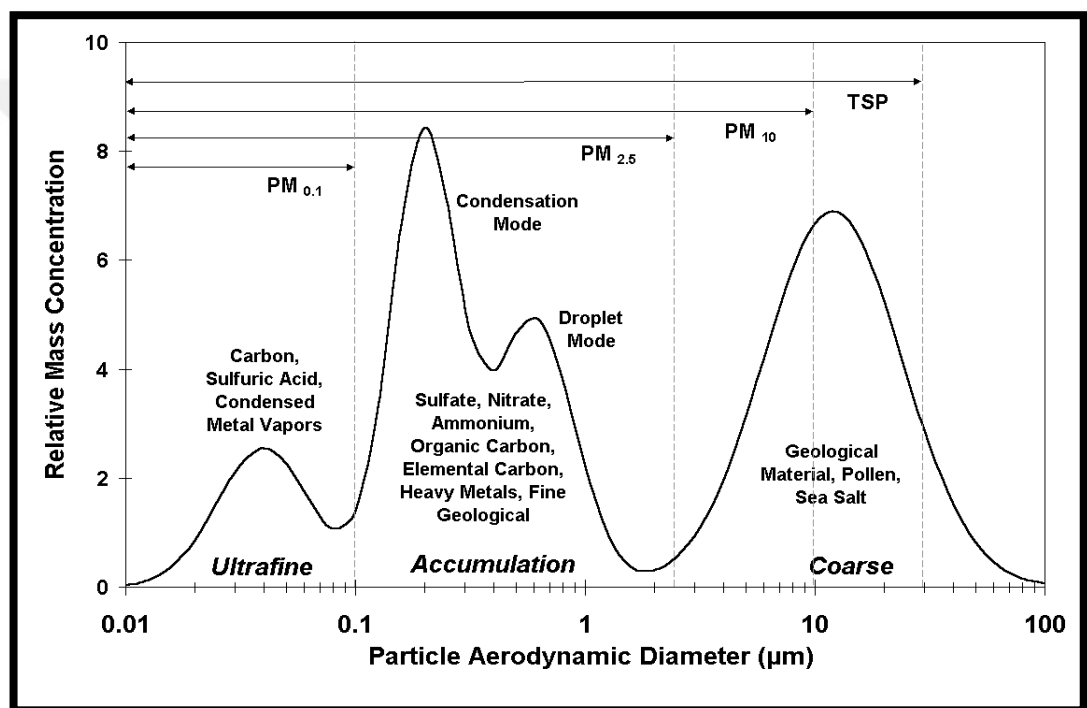


Figure 1.2. The relationship between the size and the composition of particles (Vallero, 2008)

1.3.1 Inorganic particulate matter

Water-soluble ionic compounds are major components of atmospheric aerosols. This component increases the potential health effects of fine PM (Perrone et al., 2010), reduce visibility (Tsai and Cheng, 1999) and cause terrestrial and aquatic ecosystems damage (Baker et al., 2006). The sources of those compounds are natural and anthropogenic sources such as oceans, dust storms, biomass combustion,

construction, road traffic or industrial activities, and have been commonly used for the identification of ambient PM sources (Chang et al., 2006; Gildemeister et al., 2007). As fossil fuel combustion products evolve in the atmosphere, they can react with gaseous species and produce some secondary particulate matters. For example, gaseous sulfur dioxide emitted from fossil fuel combustion and it can react both anthropogenic and biogenic species in the atmosphere to form particulate sulfate (Calvert and Stockwell, 1984).

The concentrations of trace elements are also important. They can be emitted by the processes such as erosion, surface winds, volcanic eruption, natural burning and from the oceans (Pacyna, 1998). In addition, they can be eliminated by anthropogenic processes like high temperature processes, biomass burning, fossil fuel combustion, industrial activities, and incineration, etc. (Pacyna, 1998). In a large extend, the total natural emission of trace metals to the atmosphere comes from the resuspended surface dust (e.g. more than 50% of Cr, Mn and V; more than 20% of Cu, Mo, Ni, Pb, Sb, and Zn in a global scale). Volcanic eruptions generate about 20% of Cd, Hg, As, Cr, Cu, Ni, Pb, and Sb (Pacyna, 1998). Biomass combustion contributes to Cu, Pb, and Zn levels. The most important anthropogenic sources of atmospheric Be, Co, Hg, Mo, Ni, Sb, Se, Sn, and V is combustion of fossil fuels. This combustion also affected the concentrations of As, Cr, Cu, Mn, Zn. Metallurgical processes cause emissions of As, Cd, Cu, Ni, and Zn. Lead, Fe, Zn, Ni, and Cu originated from vehicle which uses gasoline or diesel fuel. Table 1.1 shows some other sources of important elements and ions.

Table 1.1. Potential source of some important elements (Kasahara, 2012; Calvo et al., 2013, Hildemann et al., 1991; Legret and Pagotto, 1999; Garg et al., 2000; Kennedy et al., 2002; Westerlund and Johansson, 2002; Kennedy and Gadd, 2003)

Sources		Elements or ions
Secondary aerosols		SO_4^{2-} , NO_3^- , NH_4^+
Sea Salt		Cl, Na, Na^+ , Cl^- , Br, I, Mg and Mg^{2+}
Crustal or geological tracers		Si, Al, K, Na, Ca, Fe Ba, Sr, Rb, and Li. In carbonates, sulphates, oxides, hydroxides and phosphates.
Technogenic tracers	Steel industry	Cr, Ni and Mo
	Copper metallurgy	Cu and As
	Ceramic industries	Ce, Zr and Pb
	Heavy industry (refinery, coal mine, power stations)	Ti, V, Cr, Co, Ni, Zn, As and Sb
	Petrochemical industry	Ni and V
	Oil burning	V, Ni, Mn, Fe, Cr, As, S and SO_4^{2-}
	Coal burning	Al, Sc, Se, Co, As, Ti, Th, S, Pb and Sb
	Iron and steel industries	Mn, Cr, Fe, Zn, W and Rb
	Non-ferrous metal industries	Zn, Cu, As, Sb, Pb and Al
	Cement industry	Ca
	Refuse incineration	K, Zn, Pb and Sb
	Biomass burning	K and Br
	Firework combustion	K, Pb, Ba, Sb and Sr
	Vehicle tailpipe Platinum group elements	Ce, Mo and Zn
	Automobile gasoline	Ce, La, Pt, SO_4^{2-} and NO_3^-
	Mechanical abrasion of tyres	Al, Zn
	Mechanical abrasion of brakes	Al, As, Ca, Cd, Co, Cr, Fe, Ba, Cu, Sb, K, Ti, Mg, Sn, Mn, Mo, Na, Ni, Pb, Se, Sr, Zn

1.3.2 Organic particulate matter

Particulate matter (PM) is a mixture of many types of pollutants as mentioned before. Carbonaceous aerosol is one of them. It consists of particulate organic carbon (OC) and elemental carbon (EC). EC is directly emitted whereas particulate OC exists in two forms. Primary organic carbon (OC_{pri}) is directly emitted to the atmosphere, and secondary organic carbon (OC_{sec}) is formed through atmospheric oxidation of reactive organic gases and subsequent gas-to-particle conversion processes. It is important to determine the relative contributions of OC_{pri} and OC_{sec} to the ambient aerosol burden because of air quality management. (Gray et al., 1986; Turpin and Huntzicker, 1995; Strader et al., 1999; Schauer et al., 1996). However, OC is a complex mixture of hundreds of different compounds whose individual concentrations, composition, distributions, and formation mechanisms are not quantitatively understood (Turpin et al., 2000). Measurements of EC have been used to derive OC_{pri} based on the assumption that EC can serve as a tracer approach (Turpin and Huntzicker, 1995; Strader et al., 1999), because EC and OC_{pri} are both emitted directly from combustion of organic matter (Saylor et al., 2006). In this method, the OC_{pri} and OC_{sec} can be estimated as follows:

$$OC_{measured} = OC_{pri} + OC_{sec},$$

$$\text{where } OC_{pri} = OC_{non-comb} + OC_{comb}$$

OC_{comb} is calculated using the estimation of emission factor $(OC/EC)_{pri}$. The factor is relatively constant over the sampling area (Saylar et al., 2006).

$$OC_{comb} = (OC/EC)_{pri} \times EC$$

$$OC_{sec} = OC_{measured} - (OC_{non-comb} + (OC/EC)_{pri} \times EC_{measured})$$

where $OC_{measured}$ is the measured OC, OC_{pri} and OC_{sec} show the primary and secondary organic compounds, $OC_{non-comb}$ and OC_{comb} indicate the non-combustion OC (for example direct emission from vegetation) and combustion OC (Saylor et al., 2006).

It is difficult to find useful estimations of $OC_{non-comb}$. However, $(OC/EC)_{pri}$ can be estimated as the slope of the best line. The intercept is used to find $OC_{non-comb}$.

When $OC_{non-comb}$ is negligible, OC_{sec} can be calculated by using EC as the tracer for combustion source OC_{pri} (Turpin and Huntzicker, 1995).

$$OC_{pri} = ((OC/EC)_{pri} \times EC$$

$$OC_{sec} = OC_{total} - (OC/EC)_{pri} \times EC$$

If it is decided that $OC_{non-comb}$ is negligible, selection of $(OC/EC)_{pri}$ ratio is very important for the sampling site or samples. There are different approaches to select $(OC/EC)_{pri}$ in the literature using the samples concentration values. The most used three approaches are

(1) regressing measured OC versus EC data from times of low photochemical activity and dominated by local emissions;

(2) regressing measured OC versus EC data on a fixed percentile of the lowest OC/EC ratio (usually 5–20%) data to represent samples dominated by primary emissions (Lim and Turpin, 2002; Lin et al., 2009);

(3) simply taking the minimum OC/EC ratio during the study period to approximate $(OC/EC)_{pri}$ (Castro et al., 1999). EC can serve as a tracer approach (Turpin and Huntzicker, 1995; Strader et al., 1999).

1.4 Health effects of particulate matter and air quality

Particulate matter has harmful effects on humans. It is the major reason of the studying about the air pollution. Human exposure begins with the event when a person meets a pollutant of a certain concentration during a certain period (Ott, 1982).

Most research about the effect of air pollution effect on human health has centered upon respiratory and cardiovascular effects. Exposure takes place by not only

inhalation but also dermal contact with the polluted air. For example, exposure with air pollutants can result in eye or skin irritation.

PM is considered as an important air pollutant in many studies. Therefore, governments and regulations are focusing on PM, especially smaller particles. Some ambient Air Quality Standards for particulate matter was shown in different countries in different time scales are shown in Table 1.2.

1.5 Air analysis

Determination of air pollution and the effects of this pollution on human health can be found by using air analysis. Analysis of air (indoor or outdoor air) consists of three steps.

- 1) Sampling of the air
- 2) Chemical analysis of the sampled air
- 3) Quality assurance to ensure the precision and accuracy of the measurement.

In addition, sampling plan is required for the sampling of outdoor air. The plan includes the selection of proper sites based on weather condition, topography, proximity to local sources and seasonal conditions. The determination of air to be sampled, selection of the proper flow rate and measuring the flow rate accurately is also important.

Particles in the atmosphere are measured by gravimetry. The filter should be weighted before and after sampling for accuracy of the mass of the deposited particles. The collected samples are analyzed for the determination of constituents (Patnaik, 2010).

Table 1.2. Some ambient Air Quality Standards for particulate matter in different countries and different time scales

Guidelines	Sources			
	PM ₁₀ ($\mu\text{g.m}^{-3}$)		PM _{2.5} ($\mu\text{g.m}^{-3}$)	
	1 year	24 hours	1 year	24 hours
WHO (WHO, 2005)	20	50	10	25
European Union (Council Directive 1999/30/EC, 1999)	40	50		
United States (NAAQS, 2005)	50	150	15	65
California (California ambient air quality standards, 2005)	20	50	12	65
Japan (Environmental quality standards in Japan, 2006)		100		
Brazil (Conselho Nacional do Meio Ambiente, 2006)	50	150		
Mexico (Ministry of health, 2006)	50	120	15	65
South Africa (National environment management: Air Quality Act, 2004)	60	180		
India (Central Pollution Control Board, 2006) (sensitive populations /residential/industrial)	50/60/120			
China (State Environmental Protection Administration, 1996) (Classes I/II/III)	40/100/150	50/150/250		
Turkey (Anonymous 1, 2017)	40	50		

1.5.1 Preparation and analysis of samples

1.5.1.1 Preparation for analysis

1.5.1.1.1 Ultrasonic extraction

Ultrasonic extraction is a fast and simple sample treatment technique. It is generally used to make aqueous extraction for the determination of ions in PM. When the ultrasonic energy is imparted to solutions, it causes acoustic cavitation and bubbles form. Created bubbles collapse and high local temperature and pressure gradients occur in solution. On a timescale of about 10^{-10} s, effective local pressures, and energies of about 10^5 atm and about 1 eV, respectively, are generated under sonochemical conditions (Suslick et al., 1999). Sonication can also help for preparing samples directly within the sample container. Therefore, it prevents sample losses and minimizes the likelihood of sample contamination.

1.5.1.1.2 Acid digestion

PM samples must be digested with an acid or acid mixture before the analysis of metals. The salts of all metals are soluble in water. Therefore, the metals and their salts in samples are converted into their nitrate with concentrated nitric acid or the mixture of concentrated nitric acid, hydrochloric acid, sulfuric acid, perchloric acid or hydrofluoric acid although nitric acid alone is adequate for digestion of most metals (Table 1.3). A laboratory-grade microwave unit is the most preferable and quick and multi sample method to digest PM samples. The acid extract after boiling is diluted with water to a measured final volume for analysis (Patnaik, 2010).

Table 1.3. Acid combination suggested for sample preparation (Patnaik, 2010).

Acid Combination	Suggested Use
HNO ₃ - HCl	Sb, Sn, Ru and readily oxidizable organic matter
HNO ₃ - H ₂ SO ₄	Ti and readily oxidizable organic matter
HNO ₃ - HClO ₃	Difficult to oxidize organic materials
HNO ₃ - HF	Siliceous materials

1.5.2 Analysis of samples

1.5.2.1 Ion chromatography

Ion chromatography is an instrumental technique which is used for quantitative and qualitative determination of anions and cations in environmental samples. Anions (such as NO₃⁻, PO₄³⁻, SO₄²⁻, F⁻, Cl⁻, Br⁻) and cations (such as Ca²⁺, Mg²⁺, Li⁺, NH₄⁺, Na⁺, K⁺) can be determined in a single sequential step. It is simple and rapid.

The method helps separating water soluble analytes by chromatography and detect the separated ions by conductivity detector. The aqueous samples are injected into ion chromatography sampling port. Depending on the species to be analyzed, the eluent is pumped through an ion exchanger. The possible mobile phases used in ion chromatography are shown in Table 1.4. Depending on the species to be analyzed, an anion or cation guard column is used to remove organic compound and other interfering components from the samples. Anions are separated using a basic ion exchange resin while cations are separated using an acidic exchange resin. After the column, suppressor column converts the ions in the solvent into less conductive forms and the difference is measured by electroconductive detector. They are identified by the retention times and quantified by comparing the peak areas or peak height against the related calibration standards (Patnaik, 2010) (Figure 1.3).

Table 1.4. Some common eluents used in ion chromatography (Patnaik et al., 2010)

Eluents	General applications
Sodium carbonate/Sodium Bicarbonate	Common inorganic anions: F^- , Cl^- , NO_3^- , PO_4^{3-} , and SO_4^{2-}
Sodium hydroxide	Common inorganic anions: F^- , Cl^- , SO_4^{2-} ; organic anions: acetate, citrate, and fumarate
Sodium tetraborate/boric acid	Common inorganic anions: F^- , NO_3^- , SO_4^{2-} ; oxyhalides and carboxylates, such as acetate and formate
Methanesulfonic acid	Alkali and alkali earth metal ions: Na^+ , K^+ , Ca^{2+} ; ammonium
Methanesulfonic acid/acetonitrile gradient	Alkali and alkali earth metal ions; Li^+ , Na^+ , K^+ , Mg^{2+} , ammonium ion; alkyl amines: methyl amine, triethyl amine, and morpholine

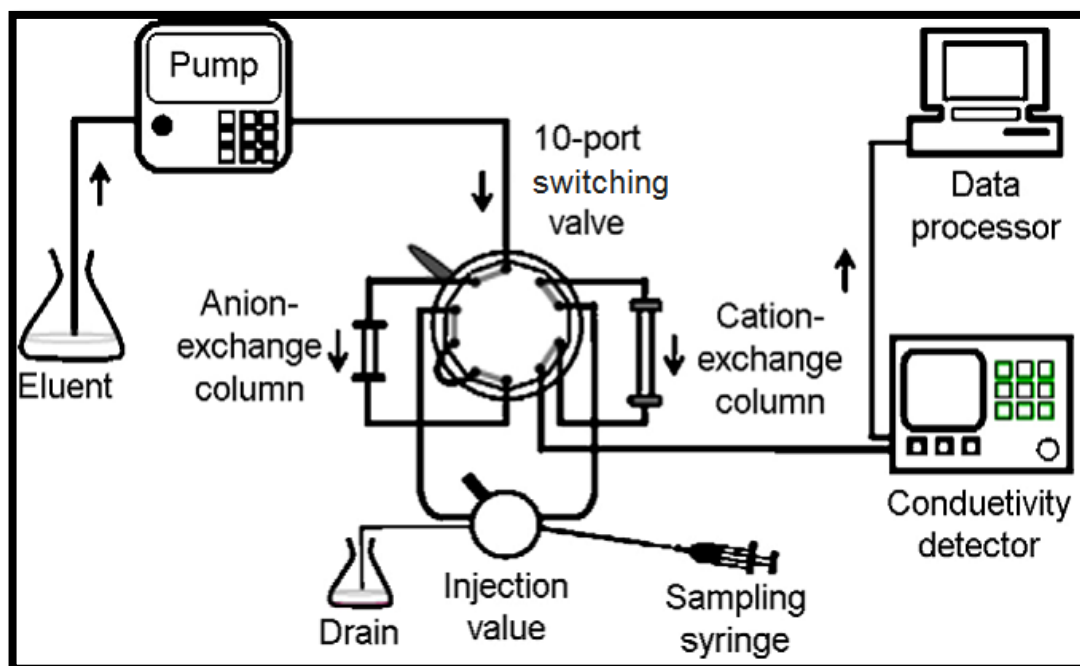


Figure 1.3. Schematic diagram of ion chromatography (Amin et al., 2008)

1.5.2.2 Inductively coupled plasma- Mass spectroscopy (ICP-MS)

Inductively Coupled Plasma- Mass Spectroscopy is an instrumental technique for determining a wide range of elements in many matrices. This technique improves sensitivity and reduce interferences (Patnaik, 2010).

In ICP-MS, the sample is aspirated through a nebulizer. It is then carried into the plasma to generate excitation. The produced ions are extracted from a vacuum pump. The ions are then separated according to their mass to charge ratio. Matrix effect, isobaric interferences and polyatomic interferences is the main reason of uncertainty (Patnaik, 2010).

The sample is typically introduced into the Inductively Coupled Plasma (ICP) as an aerosol. It is produced by passing the liquid sample through a simple pneumatic nebulizer. Larger aerosol droplets are removed by a spray chamber and the remaining smaller droplets are transported to the central channel of the argon plasma. In plasma, the bombardment of the droplets by free electrons causes the ionization of the atoms to give them a charge and ionized atoms can be identified by mass spectroscopy (Figure 1.4).

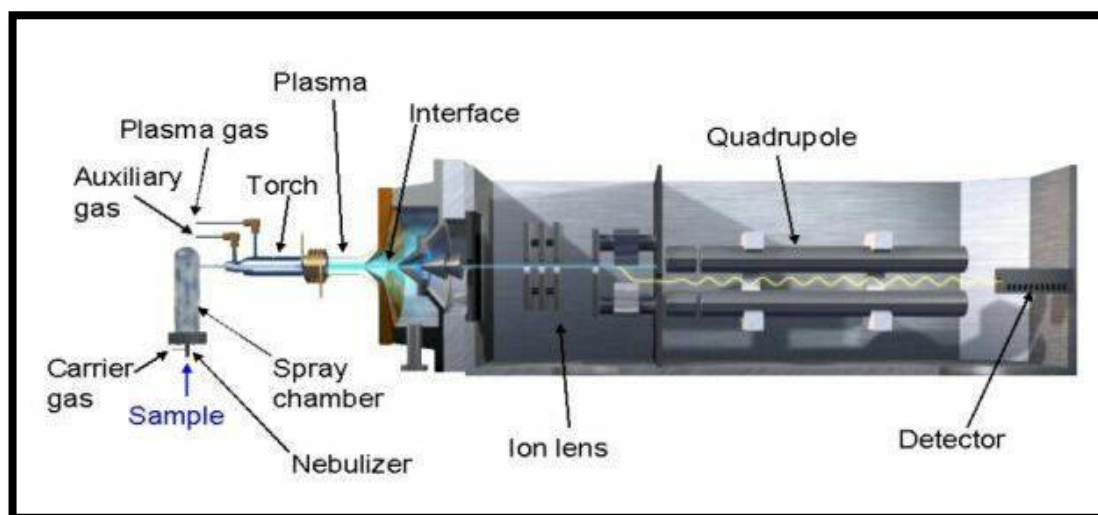


Figure 1.4. Schematic representation of ICP-MS (Anonymous 1, 2017)

1.5.2.3 Organic carbon- Elemental Carbon analyzer (OC-EC Analyzer)

OC/EC Thermal Analyzer is an instrument used for the determination of organic and elemental carbon on particles collected on quartz fiber filters. The schematic diagram of the analyzer is shown in Figure 1.5.

Samples collected on quartz filters are cut in a standard sized punch and placed in a quartz oven. When the oven is purged with helium, oven temperature increases to 870°C step by step. This temperature is desorbed organic compounds thermally and the pyrolysis products are introduced into a manganese dioxide (MnO_2) oxidizing oven. As the carbon fragments flow through the MnO_2 oven, they are quantitatively converted to CO_2 gas. The CO_2 is swept out of the oxidizing oven in the helium stream and mixed with hydrogen gas. This mixture then flows through a heated nickel catalyst. The mixture is quantitatively converted to CH_4 in this catalyst and CH_4 is subsequently measured using a flame ionization detector (FID). This is the initial temperature ramp. After the initial ramp is finished, the oven is cooled to 550°C and the flow stream is switched to an oxidizing helium/oxygen carrier gas mixture. A second temperature ramp then starts in the oxidizing gas stream and any elemental carbon is oxidized off the filter and into the oxidizing oven. The elemental carbon is then detected in the same manner as the organic carbon. After the first step, most of the OC are removed. However, some of the pyrolyzed OC in the high oven temperature make the filter darkness and causes decrease on transmittance signal. When all OC fractions are removed, the transmittance signal reaches its initial value. This point is called as split point that is used to differentiate OC and EC (Sunset Laboratory Manual, 2013).

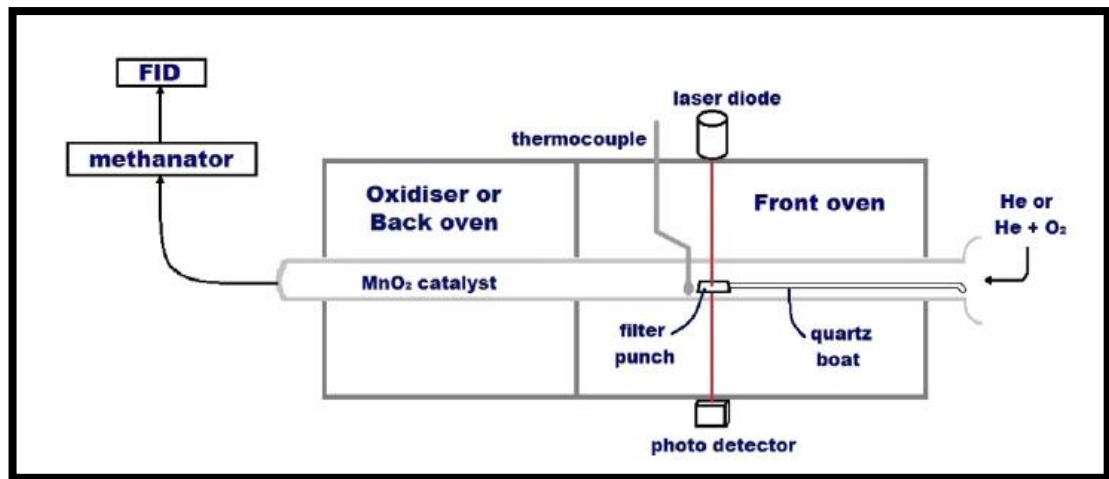


Figure 1.5. Schematic diagram of Sunset EC/OC Analyzer (Ammerlaan et al., 2015)

1.6 Statistical evaluations of data

Environmental data have inherent variability. Therefore, only limited kinds of data can be evaluated with a single analysis (Wenning and Erikson, 1994). Environmental data have several different origins. It can be affected by the environment and the experiment. As a result, the random and systematic error of environmental data requires the use of mathematical and statistical methods for further analysis (Einax et al., 1997).

1.6.1 Parameters of distribution

Similarities and differences of environmental data can be understood by environmental data. Generally, environmental data sets have high standard deviations because of the large variability of the atmospheric concentrations due mostly to meteorological conditions, physical and chemical changes, differences in sources and air mass transport patterns. In addition, the geometric mean and median values are close to each other as they show lognormal distribution (Yenisoy Karakaş, 2000).

True parameters for a distribution are not known normally. There is an estimation of observations, n . The most important parameters are the mean, the variance, and the standard deviations. Coefficient of variation or relative standard

deviation can be used for comparison. The other basic parameters which can be derive skewness and excess (kurtosis). Skewness is the one of important parameters to characterize the distribution and it is used to measure the symmetry or shape of the data. If the skewness value is 0, the data is symmetrically distributed. It can be classified also as left sided and right sided. Skewness (Sk) estimated by the symmetry of the distribution is classified as:

$Sk=0$ (symmetric)

$Sk>0$ left sided asymmetry (left sided maximum)

$Sk<0$ right sided asymmetry (right sided maximum) (Statgraph User Manual, 2006). When the standard skewness values are not between (-2) and (+2), data matrix are not normally distributed (Yenisoy Karakaş, 2000).

Kurtosis or excess (Ex) is also used to measure relative peakedness or flatness compared to a bell-shaped curve. Kolmogorov-Smirnov D statistic calculates the maximum distance between the empirical cumulative distribution function and the fitted cumulative distribution function. It helps to evaluate how plain a distribution is. When the standard kurtosis values are not between (-2) and (+2), data matrix are not normally distributed (Yenisoy Karakaş, 2000). The classification is as follows:

$Ex=0$ (normal distribution)

$Ex>0$ (the convexity of the density function is steeper than for the normal distribution)

$Ex<0$ (the convexity of the density function is smooter than the normal distribution)

The P value is the probability of finding the observed results when the null hypothesis (H_0) of a study question is true. They characterize the real shape of a normal distribution (Statgraph User Manual, 2006).

A data matrix generally shows normally distributed values and is described by using the arithmetic mean and standard deviations. This is a symmetric Gaussian distribution. However, the data set affected by different pollution sources and therefore

parameters generally follow a log-normal distribution in environmental studies (Karakaş, 1999).

1.7 Source apportionment

Source apportionment studies are used to give information about pollution sources and the amount of pollution. It has three main approaches: emission inventories, source oriented models and receptor-oriented models. Receptor oriented models (also known as receptor models) are used to characterize the measured mass of pollutants at a given site by using the multivariate analysis to solve mass balance equation. Source contributions at local and regional sites are quantified in the model. It emphasizes on the properties of the measured area. Types of receptor models are summarized in Table 1.5 (JRC reference Report, 2014).

Table 1.5. Types of receptor models

Type	Examples
Exploratory methods	Enrichment factor, Tracer method, Incremental approach
Chemical mass balance	EPA CMB 8.2
Eigenvector-based models	PCA, UNMIX
Factor analysis without constraints	FA, APCFA
Positive matrix factorization	PMF2, EPA PMF v3
Hybrid trajectory-based models	CPF, PSCF
Hybrid expanded models	PMF solved with ME-2 COPREM

1.7.1 Enrichment factor

The enrichment factor (EF) of each element is an explanatory method of receptor modelling which uses simple mathematical relationships or number of assumptions to achieve a preliminary estimation of the source contribution (JRC Reference Reports, 2014). It is calculated to understand the relative contribution of crustal and non-crustal sources. Aluminum is commonly used as a reference element

assuming that its anthropogenic sources to the atmosphere are negligible. The enrichment factor of an element X is defined by

$$EF = \frac{X_{aerosol}/Ref_{aerosol}}{X_{sources}/Ref_{sources}}$$

where, Ref is the concentration of an appropriate reference elements (e.g. Al if X derives from Earth's crust, and Na if X derives from the sea) (Hobbs, 2000).

1.7.2 Binary correlation

The Pearson product-moment correlation coefficient is a measure of the strength of the linear relationship between two variables. If the relationship between the variables is not linear, then the correlation coefficient does not adequately represent the strength of the relationship between the variables. Correlation coefficient (r) can range from -1 to 1. If two species are unrelated, r equals to zero. A correlation coefficient of -1 indicates a perfect negative linear relationship between variables and a r of 1 indicates a perfect positive linear relationship between variables (Statgraph User Manual, 2006).

1.7.3 Long range transportation (Back trajectory analysis)

Back trajectory analysis is used to get information about origin of the air masses and establish the source-receptor relationship. Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPPLIT) developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory's (ARL) is the most extensively used system which computes simple air parcel trajectories, complex transport, dispersion, chemical transformation, and deposition simulations (Draxler and Hess, 1998). The model calculation method is a hybrid between the Lagrangian approach, using a moving frame of reference for the advection and diffusion calculations as the trajectories or air parcels move from their initial location, and the Eulerian methodology, which uses a fixed three-dimensional grid as a frame of reference to compute pollutant air concentrations (the model name, no

longer meant as an acronym, originally reflected this hybrid computational approach) (Stein et al., 2015).

1.7.4 Local scale transportation

Wind sector analysis is used to get knowledge about the local sources of the pollutants. It is a common tool used to visualize the local sources. Average concentrations of the pollutants in each wind direction are taken in the analysis. A possible source of a pollutant is decided by using increase in concentration in the site. Simple pollution roses can be drawn by using concentration of pollutant. In Table 1.3, possible sources for air pollution with the directions in our sampling area are given (Öz, 2009).

1.7.5 Positive matrix factorization

Positive matrix factorization (PMF) is a multivariate factor analysis tool which uses a matrix of speciated sample data into two matrices. These are the factor contributions (G) and and factor profiles (F). The results should be interpreted by the analyst to determine the pollution sources. There are no negative source contributions in PMF. It allows each data point to be individually weighed and it helps to adjust the influence of each data point, depending on the confidence in the measurement (Norris and Brown, 2014). In addition, it uses sample concentration and associated with the sample data uncertainty which is determined by the user for individual points.

Two matrices are derived by minimizing the cost function:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]$$

where x is the data matrix of i number of samples by j chemical species which were measured and u is the uncertainties. PMF problem is solved by two common programs, PMF2 and ME-2. EPA PMF 5.0 is used ME-2 because it can solve multilinear

Table 1.6. Possible local sources for air pollution

Wind Direction	Pollutant Sources
North (N)	Traffic (E-80 and D-100 highways), Forests
North-North-East (NNE)	Traffic (E-80 and D-100 highways), Forests
North-East (NE)	Residential areas (Bolu), Agricultural areas (Karaköy), Industrial zone (Isopoly, PVC, aluminum carpentry, petrochemical, motor oil)
East-North-East (ENE)	Residential areas, Agricultural areas, Asphalt manufacturing plant
East (E)	Residential areas, Agricultural areas (Dörtdivan), Industrial zone, Leather factory (Gerede), cement factory
East-South-East (ESE)	Industrial zone (potato factories), Residential areas (Karaköy, Doğancı)
South-East (SE)	Agricultural areas (Karacasu, Seben, Kırbrıcık), Industrial zone (wood-pulp factory),
South-South-East (SSE)	Agricultural areas, Industrial zone (wood-pulp factory),
South (S)	Agricultural areas (Seben), Gölköy Lake
South-South-West (SSW)	Forest and Agricultural areas (Mudurnu, Göynük)
South-West (SW)	Agricultural areas (Mudurnu), Forest, Residential areas (Gölköy), Heating center of university (A.İ.B.Ü)
West-South-West (WSW)	Forest
West (W)	Residential areas (Bolu, Adapazarı)
West-North-West (WNW)	Traffic (E-80 and D-100 highways), Forests
North-West (NW)	Traffic (E-80 and D-100 highways), Forests, Düzce
North-North-West (NNW)	Traffic (E-80 and D-100 highways), Forests

problems including bilinear, trilinear, and mixed models. It solves the problem iteratively and this minimizes the Q .

There are two types of Q calculated by the programme, $Q_{(true)}$ and $Q_{(robust)}$. $Q_{(true)}$ is the goodness of fit parameter which is calculated by using all samples. On the other hand, $Q_{(robust)}$ is the goodness of fit parameters which is calculated by excluding samples which are the uncertainty-scaled residuals which are greater than 4. There are lots of solutions of the problem. The best solution is the lowest $Q_{(robust)}$ value along them.

Factor profiles can be affected by each PMF run. Each run must be evaluated by the user. The user must also evaluate all the error estimates. Because it helps to understand the stability of the results (Paatero et al., 2014). Variability in the PMF can be evaluated by using three methods:

- 1) Bootstrap analysis (BS)
- 2) Displacement analysis (DISP)
- 3) BS-DISP analysis

Bootstrap analysis is used to evaluate the any influence of a small set of sample results. Random error and slightly rotational ambiguity can affect the results. These errors are generally robust. There is not any influence of uncertainty which is determined by the user. DISP helps to get more sensitive results. This error interval includes only the rotational ambiguity (not including random error) However, BS-DISP is affected by both random errors and rotational ambiguity (Norris and Brown, 2014).

2. AIM AND SCOPE OF THE STUDY

Environmental problems have become a big problem with the increasing technology and human population. Air pollution is one of these problems, especially after the detection of harmful effects of air pollution on human health and ecosystem.

Particulate matter can be classified according to their chemical composition or size. Generally carbonaceous species (elemental carbon, organic carbon) elements and ions are determined in $PM_{2.5}$ and $PM_{2.5-10}$ particles. After the determination of species concentrations, the sources of pollution are evaluated with different statistical models. The results provide information about the pollution levels in the sampling area and help building policies to reduce air pollution. Therefore, the main goal of the study is to determine the elements, ions and EC and OC concentrations in $PM_{2.5}$ and $PM_{2.5-10}$ and evaluate the sources of pollution. In addition, to achieve the main goal, the study also aims,

- to validate each analytical methodology for PM analysis
- to characterize the chemical composition of PM samples,
- to determine effects of meteorological parameters on the particulate matter,
- to calculate secondary organic carbon contribution
- to compare the study with the other studies to evaluate the difference of pollution levels in Bolu atmosphere.
- to evaluate the possible sources of pollution by using receptor models (positive matrix factorization, trajectories, wind sector analysis, enrichment factor)

3. EXPERIMENTAL

3.1 Sampling area

Bolu is a city in the western Black Sea Region surrounded by Zonguldak, Karabük, Çankırı, Ankara, Bilecik, Eskişehir, Düzce and Sakarya, between 30° 32', and 32° 36', east longitudes; and 40° 06', and 41° 01', north latitudes. It has 9 districts and 512 villages (Bolu Environmental Status Report, 2010). The population of the city is 299.896 in 2016 (Anonymous 2, 2017). 53% of total population lives in the city center (Bolu Environmental Status Report, 2010).

Average altitude of the province is 1000 m while that of the city center is 725 m. There are lots of plain and lakes in this mountainous area. Total area of the province is 845.800 hectare. 149.664 hectare is used for agriculture which is 18% of the total area. Despite the small percentage of areal usage for agriculture, this city is important in agriculture for Turkey. Approximately 55% of the total area is covered by mountains (DPT, 2002). Height of mountains increases from north to south and from west to east (Bolu Environmental Status Report, 2010).

Climate of the city is like Black Sea Region and generally is warm in summer, cold in winter and rainy in all seasons. It is also affected from Marmara and central Anatolia (Bolu Environmental Status Report, 2010).

Bolu is located between Istanbul and Ankara, two important metropolis and industrialized cities. There are two highways (D-100 and TEM) connecting Anatolia to Marmara crossing in the city of Bolu (DPT, 2002).

There is lignite (Mengen – Salıpazarı Zone, Mengen – Merkezler Zone and Göynük-Himmetoğlu Zone), aluminium oxides-iron oxides (Gerede, Yeniçağa, Mudurnu), calcium oxides (Göynük), manganese oxides (Gerede), and magnesium oxides (Mudurnu) reserves in the province. Geothermal areas are used for health tourism. Food, wood products and furniture, metal industry, insulating glass and tempered glass industry, electrical equipment manufacturing, textile-clothing and

leather sector are important industries in Bolu. Industrial facilities are concentrated at the center of the city (Bolu Environmental Status Report, 2010).

There are several types of pollution sources that affect the urban and suburban air quality in Bolu. Possible major anthropogenic sources in Bolu are domestic heating, industrial and agricultural activities, and traffic. In addition, forest fires and burning of fields contribute to air pollution in this region. Mining activities especially in Mengen-Gökçesu result in land degradation and cause the environmental pollution (air, water pollution, noise) especially particulate matter pollution (Bolu Environmental Status Report, 2010).

3.2 Sampling

Sampling was performed in the campus of Abant İzzet Baysal University which is 12 km far away from the city center in 40° 42.864' north latitude and 31° 31.035' east longitude. The station was placed on the roof of presidency building (old building) (Figure 3.1).

In the sampling point, one dichotomous sampler, two particulate matter sampler and one meteorology station were placed. The sampling station point is shown in Figure 3.1. Daily aerosol samples were sampled by two types of sampler through one year period (March 2013- February 2014). Hourly data were taken from meteorology station during the whole sampling period.

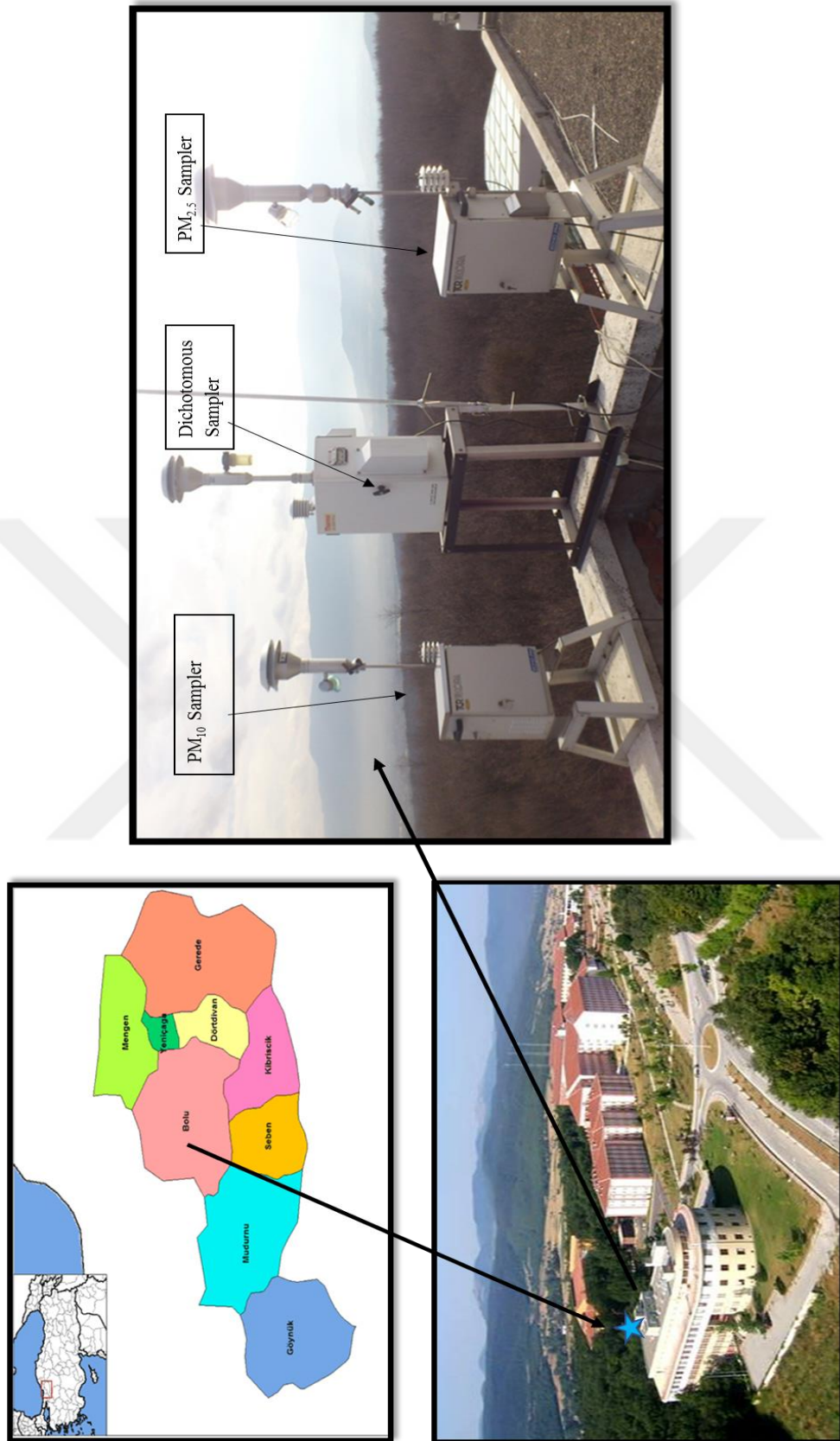


Figure 3.1. The sampling station (Anonymous 3, Anonymous 4, 2017)

3.2.1 Dichotomus sampler

Dichotomus sampler with the brand name Thermo rp Partisol® 2000-D model (Figure 3.1) is the air sampler which collects fine (particle diameter less than $2.5\ \mu\text{m}$ $\text{PM}_{2.5}$) and coarse (particles between 2.5 and $10\ \mu\text{m}$ in diameter, $\text{PM}_{10-2.5}$) PM fractions at the same time. The system collects particulate matter on two $47\ \text{mm}$ diameter filters (Whatman PTFE- $47\ \text{mm}$). Totally $16.7\ \text{L}\cdot\text{min}^{-1}$ air is introduced to Thermo Electron corporation PM_{10} inlet. The virtual impactor or dichotomus splitter which is located after the inlet, separates flow into two parts to maintain the fine particle stream at $15.0\ \text{L}/\text{min}$ and the coarse particle stream at $1.67\ \text{L}/\text{min}$. Schematic flow diagram of the instrument is shown in Figure 3.2.

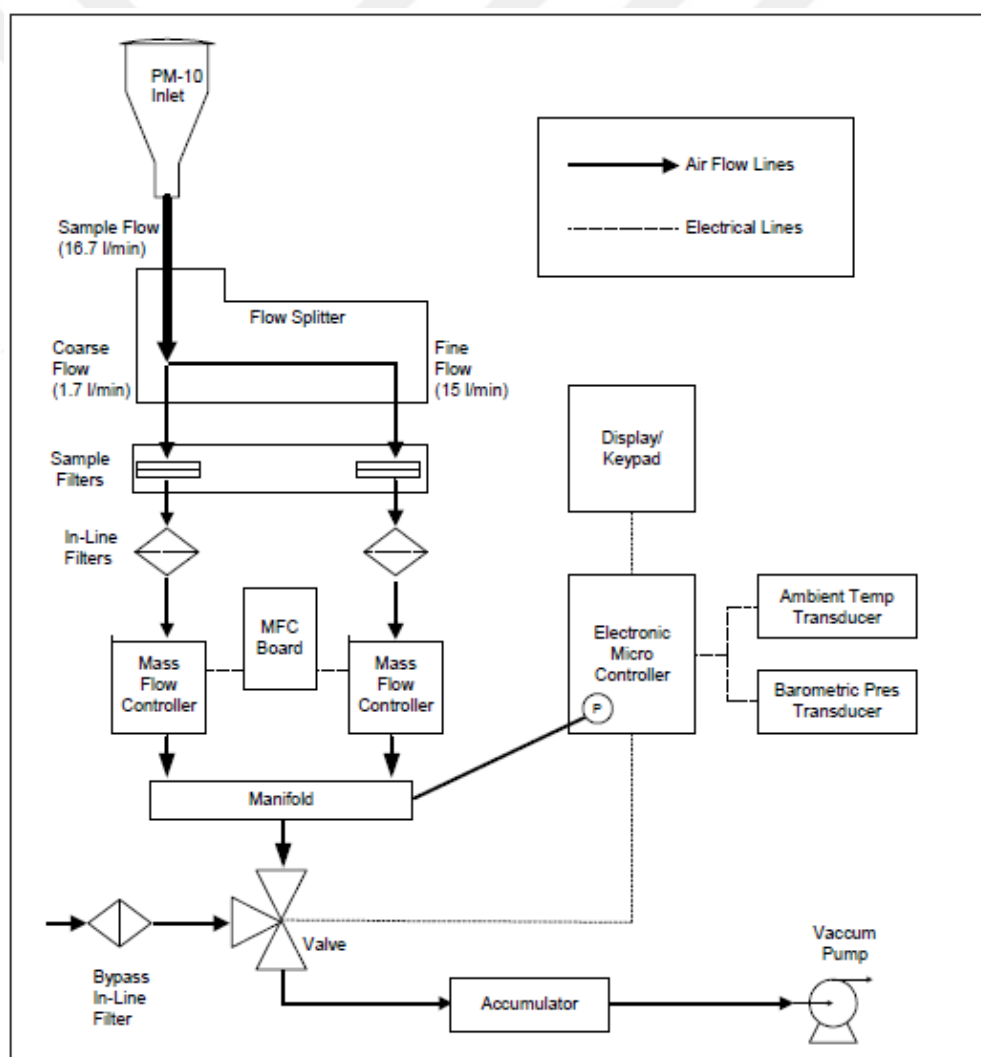


Figure 3.2. Schematic diagram of dichotomous sampler (Dichotomus Air Sampler Instruction Manual, 2015)

3.2.2 PM₁₀ and PM_{2.5} samplers

Tecora[®] atmospheric particulate matter sampler consists of seven parts: sampling head, an impactor for PM_{2.5}, filter holders, temperature and pressure sensors, pump, and control panel in body part. In this sampler, each fraction size of particles is collected individually with an air flow rate of 16.7 L. min⁻¹. The only difference of two instruments is the impactor part for PM_{2.5} particles. Impactor does not allow large particles to be collected on the filter. Therefore, this sampler is different from dichotomous sampler. The instruments are shown in Figure 3.1 (Echo PM User Manual, 2004)

3.2.3 Meteorology station

Weather Link meteorology station was used to take meteorological parameters by integrated sensors (including wind rose and rain cup). At the same time 30 parameters are measured. The parameters used in this study are shown in Table 3.1.

Table 3.1. The parameters of meteorology station used in this study

1.	Barometric pressure
2.	Humidity -high and low
3.	Rain
4.	Outside temperature-high and low
5.	Inside temperature-high and low
6.	Wind speed-high
7.	Wind direction-high

3.3 Preparation for sampling

For the sampling, two types of filters were used namely Teflon filter (Whatman PTFE-47 mm) and quartz fiber filter (Whatman Quartz-47mm). Quartz filters were baked on oven at 900°C for 3 hours to avoid the organic interferences coming from filters. The filters were conditioned in a glass cabinet located in a clean room. The condition of the clean room was set to 25% relative humidity and at 25°C. They were kept in the cabinet until the sampling time. One day before from the sampling, the filters were weighed.

3.4 Collection of samples

The filter was re-weighed and placed in the filter holders before the sampling. The prepared filters were transported to the sampling point with a special bag. Teflon filters were used in the dichotomous sampler whereas the quartz filters were used in Tecora PM samplers. After the sampling, the filter was again placed in the desiccator cabinet to remove the humidity. After waiting one day, the sampled filters were weighed and prepared for analysis.

Field blank samples were weighed and conditioned just like sample filters before and after sampling. Field blank filters were kept in the sampler for 10 seconds. They were taken from the sampler and treated as the sample filters. Laboratory blanks were also run to check any contamination in the laboratory.

Sample filters and blank samples were kept in petri dishes in the cold room (+4°C) until analysis.

3.5 Analysis of samples

3.5.1 Preparation for analysis

Whatman Teflon filters were used for the determination of elements and inorganic ionic species whereas quartz fiber filters were used to determine organic and elemental carbon.

The collected filter samples were conditioned at 25°C and at 25% relative humidity and weighed after the sampling. Teflon filters were divided into two equal parts with a clean stainless-steel bistoury. One half of the filter was used for ion determination and the other part was used for the determination of elements.

3.5.2 Determination of elements in aerosol

3.5.2.1 Reagent, chemicals, and apparatus

Firstly, reagents, chemicals and apparatus needed for element determination were provided. For the sampling, teflon filters (47 mm) were purchased from Whatman Company (USA). The samples were weighed by using analytical balance (0.1 mg) (And, Japan). Then, stainless-steel bistoury was preferred for cutting processes.

The samples were digested by using 60 % suprapure HNO₃, 40% suprapure HF from Merck Company (Germany). The digested samples were diluted in plastic centrifuge tubes. For dilution, 18.2 DI water was used. The deionized water was produced by the SG Labostar water system (Germany). Automatic pipettes with different volumes were used (5000-500 µL, 1000-100 µL, 100-10 µL) (Brand transferpette, UK). The digestion was performed by using Berghorf Speedwave® two microwave oven (Germany). SRM 1648a urban particulate matter was purchased from NIST (USA).

3.5.2.2 Analysis of samples

Filter samples (47 mm Whatman PTFE) collected by dichotomous sampler were divided into two equal parts. Half of the filter was used for the determination of elements. All glassware (volumetric flasks, forceps, and beakers) were kept in 30% HNO₃ for 24 h before analysis and then washed with deionized water several times. One half of the filters were digested in Berghof Speedwave® two microwave oven with 4 mL 60 % Suprapure HNO₃, 0.5 mL 40 % suprapure HF. In each set nine samples and one acid blank sample was run. The microwave program is given in Table 3.2. After the digestion, filter samples were taken into plastic centrifuge tubes and diluted to 25 mL with deionized water (18.2 MΩ, Ultrapure water). Digestion vessels were cleaned many times with deionized water and the washings were transferred to centrifuge tubes. Samples were analyzed by Perkin-Elmer ICP-MS (Kocaeli University). The operating parameters are given in Table 3.3. A flowchart of element analyses is shown in Figure 3.3.

Table 3.2. Microwave program

Step		1	2	3	4
Ramp	Min	5	5	5	5
Time	Min	5	10	15	15
Temperature	°C	130	170	200	220

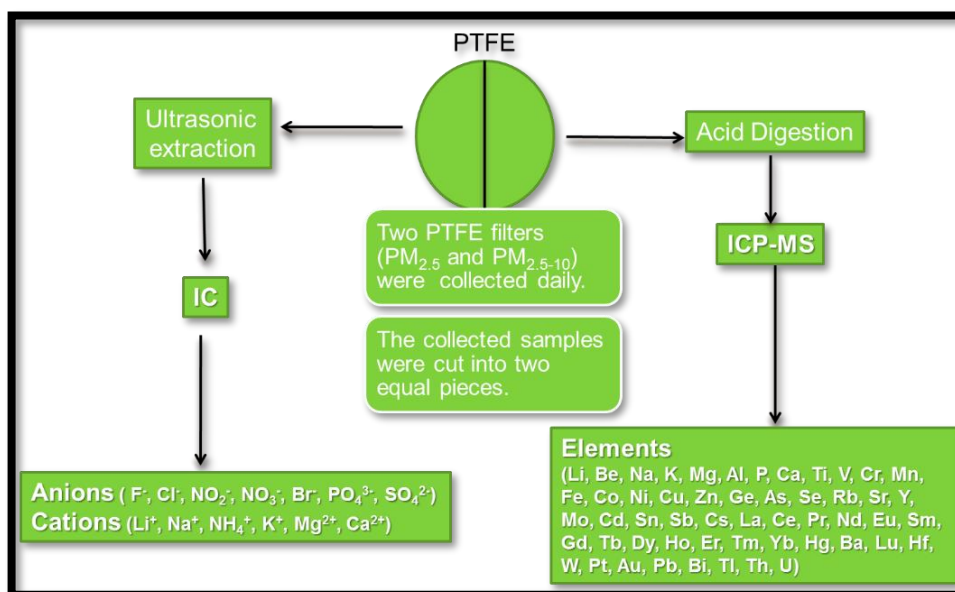


Figure 3.3. Schematic summary of ion and element determination

Table 3.3. Operating parameters of ICP-MS

Parameter	Value
RF power (W)	1300
Plasma gas flow (L min ⁻¹)	15
Auxiliary gas flow (L min ⁻¹)	1.2
Nebulizer	Gemtip crossflow
Nebulizer gas flow (L min ⁻¹)	0.96
Sampling cone (orifice dia., mm)	Platinum (1.1)
Skimmer cone (orifice dia., mm)	Platinum (0.9)
Injector	Alumina
Mass range (m/z)	5-270 amu
Spray chamber	Ryton Scott
Scanning mode	Both (analog and pulse)
Number of scans (sweeps/reading) for each isotope	20
Number of repetitions	3
Rinse time (s)	45
Sample uptake time (flush) (s)	35

3.5.2.3 Method validation studies of element determination

Element calibration standards were prepared in different ranges for each element. Calibration curves were obtained and linearity was evaluated by using r^2 values of each species. The r^2 values were higher than 0.9999. LOD and LOQ values were calculated by using the 3 and 10 times standard deviation of acid blank samples. The results were summarized in Table 3.4. Sample to blank ratios were calculated and illustrated in Table 3.5.

Table 3.4. LOD, LOQ values for elements (ng.m⁻³)

	LOD	LOQ		LOD	LOQ
Li	0.0871	0.290	Sb	0.0158	0.0527
Be	0.0232	0.0773	Cs	0.0020	0.00667
Na	30.0	99.9	Ba	4.83	16.0939
Mg	12.7	42.2	La	0.0133	0.0444
Al	107	357	Ce	0.0224	0.0747
K	8.60	28.7	Pr	0.00322	0.0107
Ca	185	616	Nd	0.00685	0.0228
Sc	0.644	2.15	Sm	0.00221	0.00737
Ti	3.95	13.2	Eu	0.00226	0.00753
V	0.290	0.967	Gd	0.00342	0.0114
Cr	10.5	35.0	Tb	0.00100	0.00333
Mn	0.924	3.08	Dy	0.00140	0.00466
Fe	126	419	Ho	0.00100	0.00333
Co	0.105	0.352	Er	0.00221	0.00737
Ni	3.99	13.3	Tm	0.00100	0.00333
Cu	1.74	5.80	Yb	0.0115	0.0383
Zn	9.66	32.2	Lu	0.00100	0.00333
Ge	0.127	0.424	Hf	0.00530	0.0177
As	0.0756	0.252	W	0.0212	0.0708
Se	0.611	2.04	Hg	0.0186	0.0621
Rb	0.0782	0.261	Tl	0.00100	0.00333
Sr	0.245	0.818	Pb	0.302	1.01
Y	0.0437	0.146	Bi	0.00663	0.0221
Mo	0.0783	0.261	Th	0.00994	0.0331
Cd	0.0139	0.0464	U	0.00884	0.0295
Sn	0.276	0.919			

Table 3.5. Sample to Blank ratios of elements

	Mean	Median	Standard deviation		Mean	Median	Standard deviation
Li	16	11	22	Sb	193	156	151
Be	2	2	1	Cs	24	19	21
Na	88	68	188	Ba	2	1	13
Mg	85	71	48	La	130	53	191
Al	142	131	107	Ce	295	106	449
K	40	29	65	Pr	23	10	34
Ca	14	10	13	Nd	61	30	102
Sc	6	4	9	Sm	10	5	16
Ti	75	56	78	Eu	4	2	16
V	98	41	269	Gd	17	8	63
Cr	35	29	25	Tb	1	1	1
Mn	39	25	48	Dy	8	4	13
Fe	4	3	4	Ho	1	0	1
Co	12	7	13	Er	5	3	8
Ni	30	15	43	Tm	2	1	2
Cu	19	11	45	Yb	5	2	8
Zn	20	16	17	Lu	2	1	2
Ge	5	3	5	Hf	22	8	128
As	72	25	143	W	10	5	14
Se	3	2	2	Hg	8	6	8
Rb	25	19	40	Tl	17	10	23
Sr	8	5	12	Pb	698	500	1153
Y	44	22	70	Bi	28	17	36
Mo	26	17	27	Th	19	10	29
Cd	22	14	23	U	9	6	11
Sn	30	25	22				

The (SRM) 1648a-UPM (Urban Particulate Matter) (NIST) was used to find the trueness of the analysis method. The SRM was weighed between 0.05 and 0.1 mg. The same digestion procedure for the samples was applied and analyzed. The results are summarized in Table 3.5.

Table 3.6. Analysis result of SRM 1648a-Urban Particulate Matter (NIST) with ICP-MS (N=8)

Parameters	Certified Value	U (k=2)	Arithmetic Mean	Standard Deviation	Error%
Na (mg/kg)	4240	60	4437	243	5
Mg (%)	0.813	0.012	0.776	0.045	-5
Al (%)	3.43	0.13	3.44	0.204	0
K (%)	1.056	0.049	0.973	0.052	-8
Ca (%)	5.84	0.19	5.64	0.383	-3
Ti (mg/kg)	4021	86	3490	225	-13
V(mg/kg)	127	11	156	7.69	23
Cr (mg/kg)	402	13	360	56.6	-10
Mn (mg/kg)	790	44	765	44.6	-3
Fe (%)	3.92	0.21	3.66	0.21	-7
Co (mg/kg)	17.93	0.68	25.2	1.71	41
Ni (mg/kg)	81.1	6.8	89.4	4.45	10
Cu (mg/kg)	610	70	557	30.6	-9
Zn (mg/kg)	4800	270	4436	226.3	-8
As (mg/kg)	115.5	3.9	114	4.06	-1
Se (mg/kg)	28.4	1.1	18.4	0.82	-35
Rb (mg/kg)	51	1.5	53.4	3.0	5
Sr (mg/kg)	215	17	255	14.4	19
Cd (mg/kg)	73.7	2.3	58.3	2.21	-21
Sb (mg/kg)	45.4	1.4	29.5	1.25	-35
Cs (mg/kg)	3.4	0.2	3.65	0.20	7
La (mg/kg)	39	3	36.7	1.84	-6
Ce (mg/kg)	54.6	2.2	51.8	2.57	-5
Sm (mg/kg)	4.3	0.3	3.45	0.19	-20
W (mg/kg)	4.6	0.3	6.61	0.54	44
Pb (%)	0.655	0.033	0.637	0.04	-3

3.5.3 Determination of ions

3.5.3.1 Reagent, chemicals, and apparatus

Ultrasonic extractions were performed by using an ultrasonic bath (Bandelin, Germany). An oven (Binder, Turkey), (0-250°C), was used to dry glasswares. The deionized water was produced by the SG Labostar water system.

Column, guard column and suppressor properties are given in Table 3.6. Sodium carbonate and methane sulfonic acid were used as a mobile phase in ion chromatography and purchased from Sigma Aldrich (Germany). Calibration standard solutions (anion mix seven components and cation mix six component) were purchased from Thermo Fisher Scientific (USA). Intermediate stock solutions were prepared from the main stock standards with appropriate dilutions with deionized water. ERM-CA408 simulated rainwater (low contents) was purchased from LGC Standards (UK).

All stock, intermediate and standard solutions were stored in a refrigerator. Automatic pipettes with different volumes were used to prepare standards in 5 mL vials. (5000-500 µL, 1000-100 µL, 100-10 µL) (Brand transferpette, UK).

3.5.3.2 Analysis of samples

One half of the 47 mm Whatman PTFE filter was used for ion determination. Filter samples were extracted with 7 mL deionized water in ultrasonic water bath for 1 hour. Then, extracts were filtered with 0.22 µm cellulose acetate filter and prepared for analysis. Before sample analysis, standard Dionex anion mix and Dionex cation mix were used for calibration. Ion determination in aerosol samples was performed by using Dionex ICS 1100 series ion chromatography. Operating conditions of the instrument are given in Table 3.6.

Table 3.7. Optimum operation conditions for Dionex ICS 1100 Ion Chromatography

	Anion	Cation
Mobile phase	9 mM Na ₂ CO ₃	20 mM Methanesulfonic acid
Column	Ionpac AS9-HC (250 x 4 mm)	Ionpac CS12-A (250 x 4 mm)
Guard column	Ionpac AG9-HC (50 x 4 mm)	Ionpac CG12-A (50 x 4 mm)
Suppressor	ASRS-4 mm	CSRS-4mm
Suppressor current	45 mA	65 mA
Detector	Conductance detector	Conductance detector
Pressure (psi)	2000-3000	2000-3000
Oven temperature	30 °C	30 °C
Background conductance	< 30 µS	0.5-2 µS
Flow rate	1.00 mL/min	1.00 mL/min
Injection volume	500 µL	1000 µL
Rate of data transfer	5.0 Hz	5.0 Hz
Duration	30 min	15 min

3.5.3.3 Method validation studies of ion determination

Anion working solutions were prepared between the ranges of 0.5 ppm- 50 ppm. The total anion chromatogram was completed in 30 minutes. On the other hand, cation working solutions were prepared in the range of 0.05 ppm- 7.5 ppm. The total cation chromatogram was completed in 15 minutes. Five-point calibration curves were prepared (Figure 3.4. and Figure 3.5). Linearity was evaluated by using r^2 values. The r^2 values were higher than 0.9959. Detection limits were calculated by ten replicates of standard solution in lower regions of the calibration curve. LOD values are the 3 times standard deviation of ten replicates, LOQ values are the ten times standard deviation of ten replicates. The results were summarized in Table 3.7.

The trueness of results was checked by using the ERM-CA408 simulated rainwater (low contents). The standard was analyzed without any dilution. The results are summarized in Table 3.8.

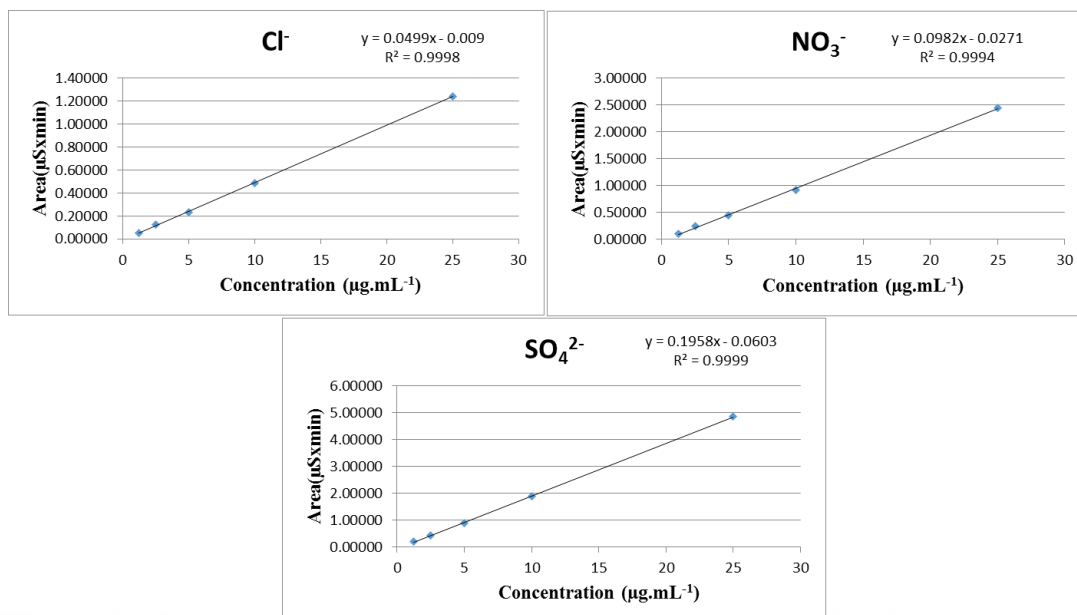


Figure 3.4. Calibration curves for anions

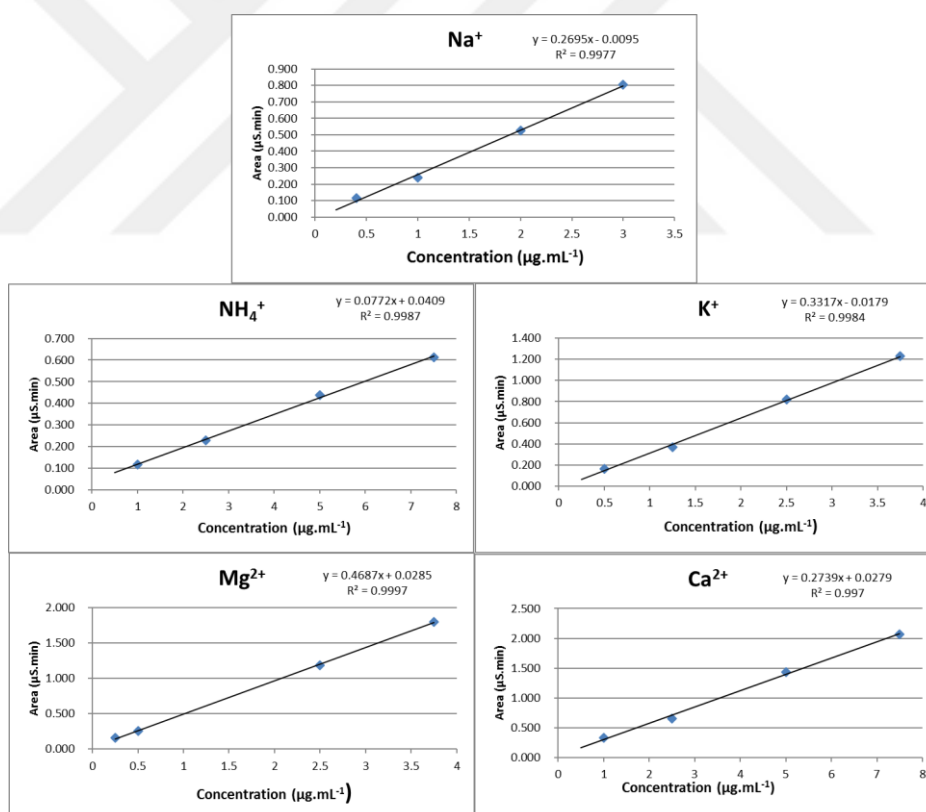


Figure 3.5. Calibration curves for cations

Table 3.8. Linearity, R^2 , LOD, LOQ values for ions

	Linearity ($\mu\text{g L}^{-1}$)	R^2	LOD ($\mu\text{g.mL}^{-1}$)	LOQ ($\mu\text{g.mL}^{-1}$)
Cl^-	1.25-25	0.9998	1.55	5.16
NO_3^-	1.25-25	0.9994	2.96	9.88
SO_4^{2-}	1.25-25	0.9999	0.95	3.15
NH_4^+	0.50-7.5	0.9959	0.022	0.073
Na^+	0.20-3.0	0.9981	0.044	0.147
K^+	0.25-3.75	0.9986	0.049	0.162
Mg^{2+}	0.25-3.75	0.9996	0.021	0.071
Ca^{2+}	0.5-7.5	0.997	0.116	0.385

Table 3.9. ERM-CA408 simulated rainwater (low contents) results (N=10)

	Certified value (mg/L)	U (k=2)	Aritmetic mean (mg/L)	Standard deviation	Error%
NH_4^+	0.91	0.028	0.789	0.0387	-13.3
Mg^{2+}	0.145	0.022	0.113	0.0122	-21.7
F^-	0.194	0.008	0.187	0.00481	-3.15
Cl^-	1.96	0.07	1.94	0.0135	-0.73
NO_3^-	2.01	0.09	1.97	0.0211	-1.70
SO_4^{2-}	1.46	0.04	1.49	0.0291	2.39

3.5.4 Determination of TC/EC/OC

3.5.4.1 Reagent, chemicals, and apparatus

Quartz microfiber filters (47 mm) were from Whatman Company (USA). A muffle furnace (Boyut, Turkey) was used to remove organics from the quartz filter. Suprapure HCl from Sigma Aldrich (USA) was used to determine carbonates from samples. All standard solutions were stored in a refrigerator at 4°C. An oven (Binder, Turkey), (0-250°C), was used to dry glasswares. An analytical balance (0.1 mg) (And, Japan) was used for all weighing processes.

3.5.4.2 Analysis of samples

For the determination of carbonaceous species in the quartz filter, Sunset EC/OC thermal analyzer was used. Firstly, sampled quartz filters were weighed. A standardized size (1x1.5 cm) punch is cut from that filter and placed in the oven. Temperature profile of NIOSH 870 method was shown in Table 3.9. Sample thermogram of NIOSH 870 is shown in Figure 3.6. For carbonates determination, one punch of sample was waited in a petri dish containing 30% HCl acid fume for 3 hours.

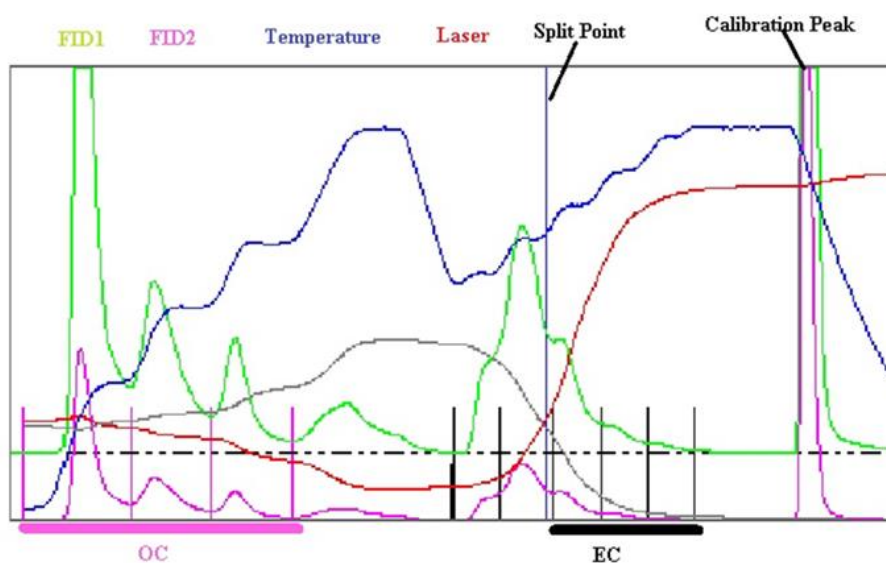


Figure 3.6. Sample thermogram of NIOSH 870

Table 3.10. Temperature profile of NIOSH 870

Mobile phase	Time (s)	Temperature (°C)
Helium	10	1
Helium	80	310
Helium	80	475
Helium	80	615
Helium	110	870
Helium	45	550
Oxygen	45	550
Oxygen	45	625
Oxygen	45	700
Oxygen	45	775
Oxygen	45	850
Oxygen	110	870
Calibration gas CH ₄	120	1
Offline	1	0

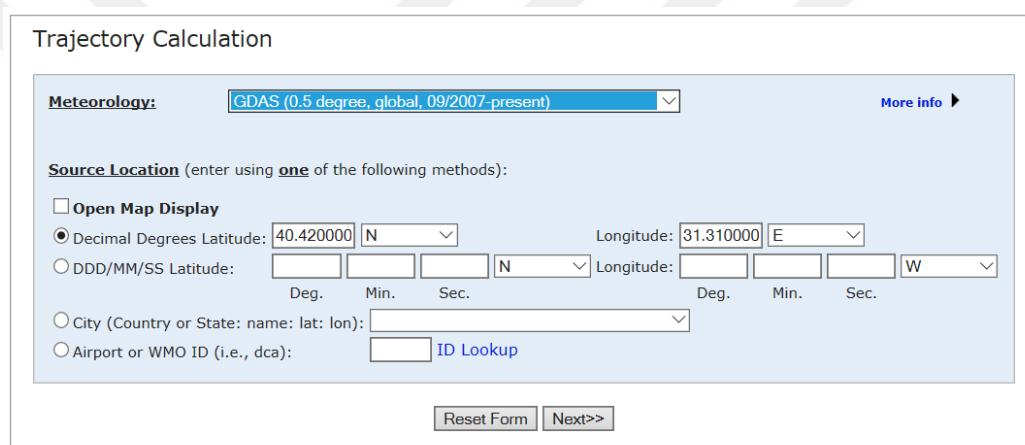
3.5.4.3 Method validation studies of EC-OC analysis

Acetanalide solution was used to calculate the relative error of the analysis in every five samples. A punch (1.5 cm²) was cut from a clean quartz filter and 10 µL of the standard was pipetted to 1.5 cm² filter. The arithmetic mean of relative error of applied acetanalide standards (n= 40) was determined as 6.73%. Calibration was reperformed in the change of methane gas tank. The method detection limit (MDL) was calculated for both EC and OC by 3 times standard deviation of concentrations of eight filter blank samples. MDLs of OC and EC were determined as 4.02 and 0.060 µg.cm⁻², respectively.

3.6 Usages of source apportionment softwares

3.6.1 Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT)

HYSPLIT model was used to take information about long range transportation. The model runs in the website of <http://ready.arl.noaa.gov/HYSPLIT.php>. First, 'Run HYSPLIT Trajectory Model' were selected and then the software compute the trajectories by using archive data. Only one source location was selected. Then, the coordinates of the sampling point should be entered to the program (Figure 3.7.)



The screenshot shows the 'Trajectory Calculation' web form. At the top, there is a 'Meteorology' dropdown menu set to 'GDAS (0.5 degree, global, 09/2007-present)' with a 'More info' link. Below this is the 'Source Location' section, which instructs the user to enter coordinates using one of four methods. The first method, 'Decimal Degrees Latitude', is selected with radio buttons. It shows input fields for Latitude (40.420000) and Longitude (31.310000), each with a directional dropdown (N and E respectively). The second method, 'DDD/MM/SS Latitude', shows empty input fields for Degrees, Minutes, and Seconds, and a directional dropdown (N). The third method, 'City (Country or State: name: lat: lon)', shows an empty dropdown menu. The fourth method, 'Airport or WMO ID (i.e., dca)', shows an empty input field and an 'ID Lookup' link. At the bottom of the form are 'Reset Form' and 'Next>>' buttons.

Figure 3.7. The screen in which the user writes the coordinates of the sampling point in the HYSPLIT model

After the selection of the date, trajectory direction, vertical motion, total run time, and levels which were selected. In our study, the backward analysis for 72 hours (total run time) was selected for each day to analyze sources of pollution. Isentropic option was selected to eliminate any temperature- induced change. Three levels (500, 1500 and 3000 m) were analyzed to evaluate local and regional air masses (Figure 3.8). Finally, a figure was taken as in Figure 3.9 and interpreted. This figure also gave the information about the selected options.

Model Parameters

Trajectory direction: ☐ Forward ☒ Backward (Change the default start time!) [More info](#)

Vertical Motion: ☐ Model vertical velocity ☐ Isobaric ☒ Isentropic [More info](#)

Start time (UTC): Current time: 16:31
 year: 13 month: 04 day: 07 hour: 11 [More info](#)

Total run time (hours): 72 [More info](#)

Start a new trajectory every: 0 hrs **Maximum number of trajectories:** 24 [More info](#)

Start 1 latitude (degrees): 40.420000 [More info](#)

Start 1 longitude (degrees): 31.310000 [More info](#)

Start 2 latitude (degrees):

Start 2 longitude (degrees):

Start 3 latitude (degrees):

Start 3 longitude (degrees):

Level 1 height: 500 ☒ meters AGL ☐ meters AMSL [More info](#)

Level 2 height: 1500

Level 3 height: 3000

Figure 3.8. The trajectory direction, vertical motion and total run time selection screen in HYPPLIT

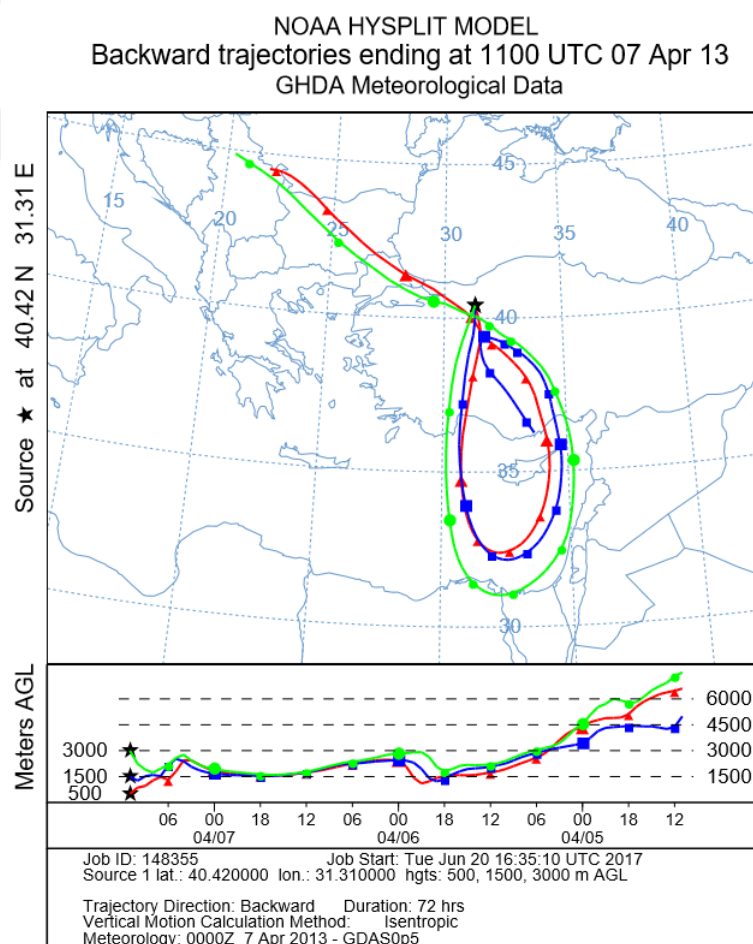


Figure 3.9. A sample result of trajectory analysis

3.6.2 PMF version 5.0

The program was downloaded from the website of EPA. The first window was Data Files under the Model Data tab (Figure 3.10). The screen had three sections: Input Files, Output Files, and Configuration File. Two types of input files are required.

1. Sample species concentration values
2. Sample species uncertainty values

Figure 3.10 The first window of PMF program

The concentration file can not include blank cells. Therefore, those cells were filled with the MDL/2. If there are outliers in a data set, the outliers are deleted and the deleted cells are filled with median values.

In uncertainty file, zeros and negative values are not permitted as an uncertainty. In addition, sample number and species number must be same with the

uncertainty file. There are two possible calculations in an uncertainty file. If the concentration is greater than the MDL, the uncertainty is calculated as below:

$$Unc = \sqrt{(Error\ fraction \times concentration)^2 + (0.5 \times MDL)^2}$$

If the concentration was lower than the MDL, the uncertainty was calculated as 5/6 times MDL of the species. If there were deleted species cell in a sample because of error of an analysis, the uncertainty was four times geometric mean. A sample of concentration file is shown in Figure 3.11.

Dates	Li	Be	Na	Mg	Al	K	Ca	Sc	Ti	V
1.03.2013	0.204324291	0.002126	279.749	248.505	738.594	55.503	1882.92	0.41523	18.8546	0.59164
2.03.2013	0.030699075	0.002126	173.34	209.9	488.522	4.2983	238.472	0.35965	5.74419	0.12472
3.03.2013	0.097173755	0.0060178	177.82	220.233	1117.76	4.2983	529.783	0.86806	6.41538	0.13266
4.03.2013	0.165099961	0.002126	309.871	258.803	875.714	49.6008	874.118	0.70642	14.6306	0.70409
6.03.2013	0.050948567	0.002126	233.323	209.63	613.232	4.2983	189.742	0.37508	6.34874	0.08835
21.03.2013	1.367808223	0.05372056	459.854	583.197	1774.26	382.984	2069.19	1.14673	85.9095	2.39676
22.03.2013	0.187475004	0.02060165	266.936	273.485	873.314	58.5705	507.213	0.53976	18.8196	0.5377
23.03.2013	0.106733627	0.002126	257.885	269.967	15391.2	58.8833	975.203	0.62917	11.0048	1.51112
24.03.2013	0.72785985	0.002126	384.035	339.118	1196.39	238.996	2127.56	0.85042	25.1249	1.47073
26.03.2013	0.934753464	0.002126	630.441	552.225	1857.95	358.766	1949.44	0.97159	81.6367	2.40826
29.03.2013	0.075133375	0.002126	173.437	238.878	811.977	45.3075	467.43	0.52593	8.95757	0.24418
30.03.2013	0.187573166	0.002126	166.076	257.209	11800.3	84.3616	622.313	0.20654	16.498	1.40364
31.03.2013	1.082390902	0.03594656	595.005	745.572	1827.75	404.507	4119.54	0.98853	85.0795	3.74244
1.04.2013	0.972244164	0.04589994	357.137	397.114	916.538	230.374	2322.82	16.6387	44.3227	29.3614
2.04.2013	0.417567341	0.002126	245.923	493.109	591.792	125.785	1521.98	1.68817	28.6809	35.6046

Date	Li	Be	Na	Mg	Al	K	Ca	Sc	Ti	V
1.03.2013	0.220726	0.002126	284.9713	272.6084	864.0994	260.2776	304.0435	0.682872	9.714253	0.56791
2.03.2013	0.161708	0.002414	256.1063	293.415	3009.742	22.31325	645.1847	1.158503	8.674289	0.337897
3.03.2013	0.296454	0.006588	589.7896	359.3856	1150.909	84.38396	1142.077	1.089194	20.83522	0.764192
4.03.2013	0.198653	0.009574	356.3183	301.4495	902.6683	238.5628	547.2212	1.280472	10.61954	2.182786
6.03.2013	0.04169	0.002126	226.4	258.3812	806.9603	4.298301	426.0115	0.963513	8.057837	0.055587
5.04.2013	0.153596	0.029256	199.0407	212.0305	520.1657	49.21162	652.0193	0.646078	14.67937	35.85366
6.04.2013	0.996567	0.002126	385.8533	649.4548	1963.261	423.0923	2951.584	1.119367	77.50317	1.516104
7.04.2013	0.308173	0.002126	404.2665	471.1613	1346.547	179.9707	1766.97	2.086637	11.9764	2.754737
8.04.2013	0.04353	0.002126	152.7358	136.1018	461.3914	13.23014	682.8681	0.312737	5.604338	0.118907
9.04.2013	0.04353	0.002126	242.1405	285.8044	854.6448	59.94931	522.9358	0.561987	10.60444	17.36294

Figure 3.11. An examples of concentration and uncertainty file

After the concentration and uncertainty file was uploaded to the program, input and output specifications were performed. Figure 3.12 shows the concentration/uncertainty screen. The default value for all the species is ‘Strong’. A categorization is done by the user. The user must categorize the S/N ratios as ‘Bad’ if the S/N ratio is less than 0.5 and weak if the S/N ratio is between 0.5 and 1. Secondly, the concentration time series screen, the greatest and lowest values in each samples

was excluded from the program. The data exception part gives information about the samples which were excluded and the species which are categorized as ‘Bad’, ‘Weak’ and ‘Strong’.

Base model studies were started after categorization and exclusion of samples. Figure 3.13 shows base model run screen. In this screen, number of runs, number of factors, and seed number must be selected. Number of runs means that the number of base runs to be performed. The recommended run number is 20. Because this number helps assessing the variation of Q. Number of factor is judged by experienced user. Making a good estimate of number of factors is based on engineering intuition. Besides, a preliminary factor analysis can be performed to make a good estimate. Finally, seed is the starting point for each iteration in ME-2. Choosing random initials is a good choice. However, the seed number must be noted by the user to take the same results from the same sample data. The recommended seed number is 25.

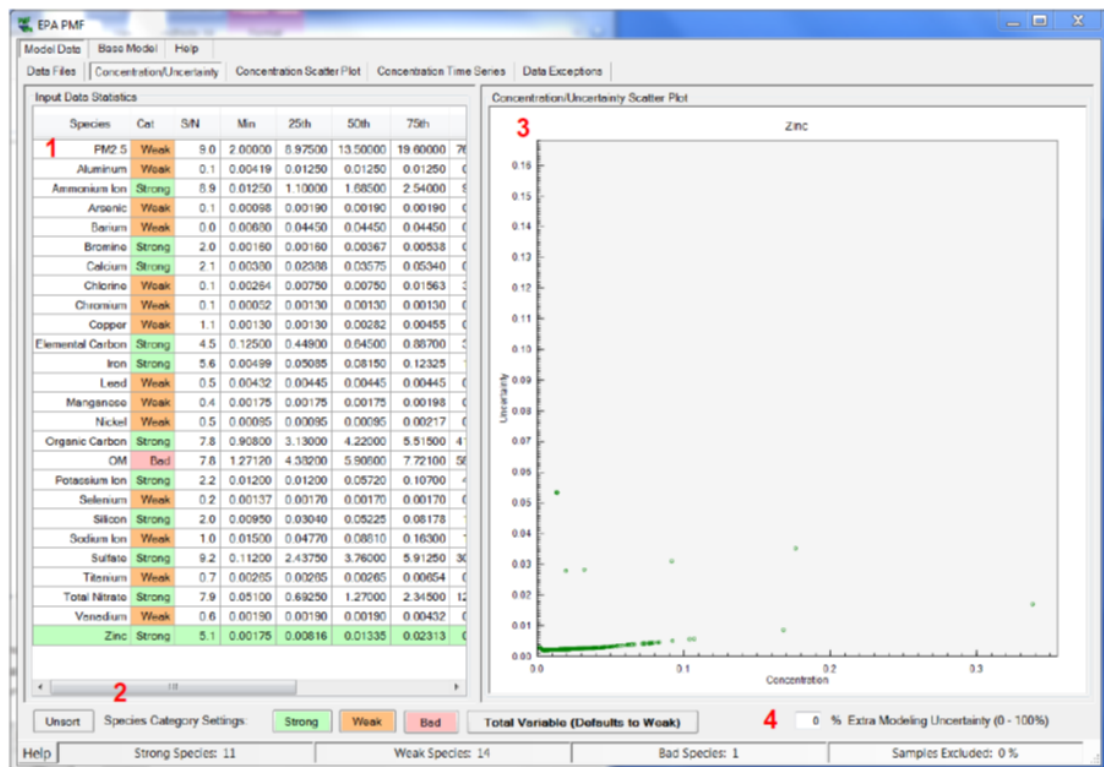


Figure 3.12. Concentration/Uncertainty screen

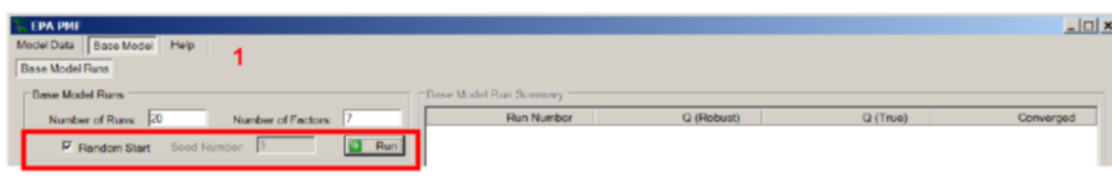


Figure 3.13. Base model screen

A summary is shown in the screen after the base run is completed (Figure 3.14). The lowest Q_{robust} is highlighted by the programme. Q_{robust} must be about 10% lower than the Q_{true} . In addition, $Q_{\text{theoretical}}$ must be calculated by the equation:

$$Q_{\text{theoric}} = n m - p (n+m)$$

where n is the number of samples m is the number of species (strong and weak) and p is the number of factors.

$Q_{\text{robust}}/Q_{\text{theoretical}}$ value must be lower than 1.5. After this magnitude obtained by the model, base model results were evaluated. In residual analysis screen, the histogram shows how well the model fit to each species. All residuals must be between +3 and -3. If the residual for any species is high, it may be an indication of poor fitting of model. Observed/predicted scatter plot helps to compare observed and predicted values. Good correlation of values is evaluated by the help of r^2 values. If r^2 values are low for a strong species, the user must return to the model data screen and categorize the strong species as a weak and model must be rerun. In Profiles/Contribution screen, the profile graph shows the concentration of each species apportioned. Factor fingerprints screen helps to verify factor names and determine the distribution of species in each factor. G-space plot screen helps to understand any relationships between two different factors. Factor contribution screen shows the distributions of each species in each factor. After well-fitted model is obtained, base model results are taken and interpreted (Norris and Brown, 2014).

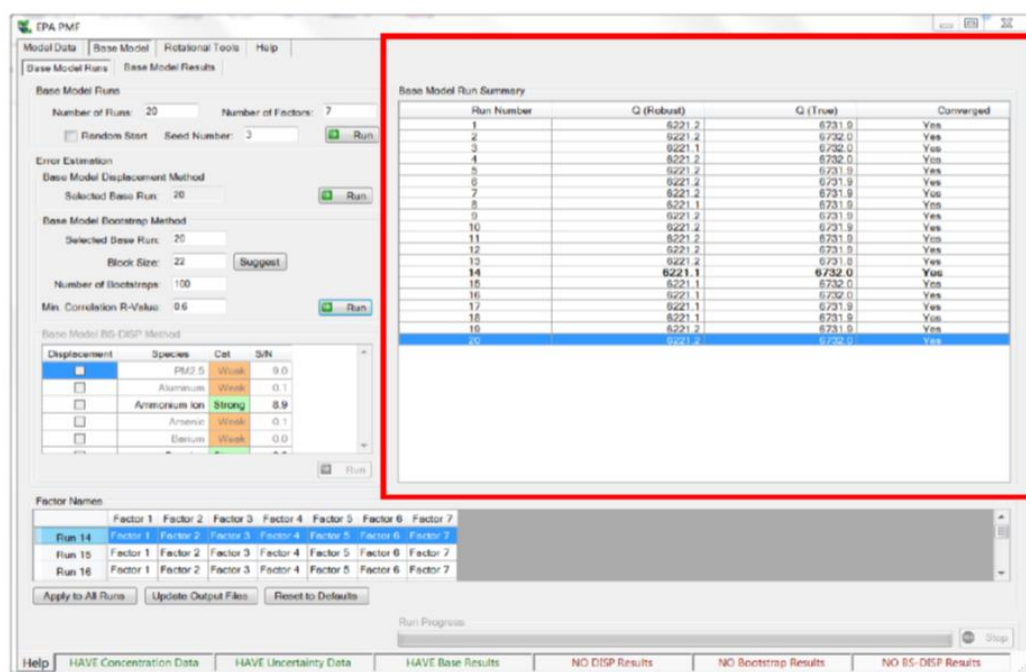


Figure 3.14. Base model result screen

After the factor profiles are evaluated and taken good correlation between the factor profiles and results, error estimation, base model displacement model and base model BS-DISP method are evaluated.

4. RESULTS AND DISCUSSIONS

4.1 General information of samples

For the determination of inorganic species, a total of 326 PM_{2.5-10}, and 312 PM_{2.5} samples were collected. While 172 PM₁₀ and 166 PM_{2.5} samples were collected for EC/OC measurement. The samples were collected within the campus of Abant İzzet Baysal University between March 2013 and February 2014. Teflon filters were used to determine anions (Cl⁻, NO₃⁻, SO₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) and elements (Li, Be, Na, K, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hg, Ba, Hf, W, Pb, Bi, Tl, Th, U). The measured concentrations of each parameter were evaluated statistically, temporally and seasonally.

In PM_{2.5}, the most observed elements were Na, Mg, Al, Ca, Sc, Ti, Cr, Ce, Zn, Rb, Pb (Table 4.1). Aluminium, Ca, Na, Fe, Mg, and K had the highest arithmetic mean concentrations. However, Al, Ca, Na, Mg, Fe, K had also the highest geometric mean concentrations, respectively. Calcium had the highest standard deviation. The most observed anion and cation were Na⁺ and Cl⁻. Sulfate and Ca²⁺ had the highest arithmetic and geometric mean concentrations. OC concentrations were higher than EC concentrations.

Table 4.1. Statistical evaluation of measured parameters in PM_{2.5} aerosols (ng.m⁻³)

	N	Aritmetic mean	Median	Geometric mean	Standard deviation	Min	Max
Li	228	0.217	0.146	0.143	0.258	0.00977	2.18
Be	49	0.0228	0.0240	0.0180	0.0121	0.00138	0.0556
Na	253	412	289	284	1115	6.36	14962
Mg	253	298	278	257	223	8.30	2901
Al	253	1020	898	911	647	9.44	7063
K	248	172	117	115	342	4.45	4908
Ca	253	715	429	446	1189	11.4	14099
Sc	253	0.774	0.610	0.599	0.924	0.0460	8.46
Ti	253	12.7	9.76	10.4	11.0	0.540	88.3
V	252	1.39	0.800	0.772	3.68	0.0328	42.0
Cr	253	34.3	31.3	26.4	43.0	0.491	564
Mn	252	4.76	2.97	2.84	8.19	0.0302	87.7
Fe	240	300	249	219	349	2.56	4668
Co	250	0.278	0.141	0.148	0.456	0.00454	4.54
Ni	249	7.10	3.15	3.25	15.3	0.0638	170
Cu	250	3.09	2.30	2.16	3.64	0.0592	41.3
Zn	253	16.7	11.8	11.9	17.8	0.480	173
Ge	187	0.105	0.0574	0.0630	0.132	0.00140	1.16
As	253	2.44	0.810	0.944	5.19	0.00144	54.5
Se	204	0.472	0.344	0.326	0.480	0.00860	3.19
Rb	253	0.493	0.348	0.330	1.21	0.0115	18.7
Sr	250	1.43	0.708	0.768	4.18	0.0200	62.3
Y	248	0.0492	0.0225	0.0272	0.104	0.00267	0.956
Mo	226	0.405	0.281	0.258	0.569	0.0208	5.75
Cd	239	0.158	0.125	0.114	0.151	0.00698	1.67
Sn	251	0.564	0.423	0.423	0.465	0.0197	3.37
Sb	252	0.404	0.323	0.297	0.403	0.0162	4.95
Cs	252	0.0524	0.0422	0.0397	0.0474	0.00227	0.516
Ba	252	23.2	4.56	4.54	269	0.0691	4270
La	252	0.176	0.0581	0.0844	0.311	0.00431	3.45
Ce	253	0.408	0.109	0.177	0.791	0.0115	9.20
Pr	247	0.0282	0.0102	0.0143	0.0455	0.00134	0.383
Nd	251	0.0680	0.0303	0.0363	0.127	0.00144	0.926
Sm	234	0.0115	0.00521	0.00659	0.0205	0.00133	0.159
Eu	160	0.00903	0.00245	0.00332	0.0581	0.00128	0.735
Gd	223	0.0276	0.00739	0.00907	0.197	0.00140	2.94
Tb	98	0.00329	0.00149	0.00227	0.004218	0.00128	0.0264
Dy	239	0.00899	0.00464	0.00502	0.017043	0.00131	0.130
Ho	117	0.00342	0.00150	0.00228	0.00503	0.00128	0.0337
Er	217	0.00624	0.00243	0.00349	0.014189	0.00128	0.157
Tm	35	0.00386	0.00220	0.00262	0.004744	0.00130	0.0247
Yb	210	0.00625	0.00246	0.00342	0.01614	0.00133	0.182

Table 4.1. Statistical evaluation of measured parameters in PM_{2.5} aerosols (ng.m⁻³) (continued)

	N	Aritmetic mean	Median	Geometric mean	Standard deviation	Min	Max
Lu	38	0.00395	0.00222	0.00251	0.00607	0.00130	0.0337
Hf	245	0.0404	0.00864	0.00933	0.297	0.00141	3.973
W	216	0.164	0.0820	0.0828	0.340	0.00237	3.055
Pt	5	0.00851	0.00697	0.0055	0.00774	0.00136	0.0202
Au	18	0.0769	0.0426	0.0374	0.0770	0.00240	0.241
Hg	216	0.0472	0.0349	0.0264	0.0755	0.00131	0.939
Tl	226	0.0527	0.0335	0.0323	0.0745	0.00236	0.727
Pb	255	5.220	3.66	3.43	8.01	0.0704	105
Bi	231	0.0784	0.0437	0.0458	0.0984	0.00230	0.754
Th	252	0.0257	0.0132	0.0154	0.0537	0.00145	0.527
U	249	0.0135	0.00794	0.00897	0.0201	0.00140	0.211
Cl⁻*	249	2.34	1.67	1.98	1.58	0.507	11.4
NO₃⁻*	244	0.278	0.187	0.174	0.276	0.0253	2.45
SO₄²⁻*	219	6.24	2.19	2.49	8.97	0.196	43.8
NH₄⁺*	224	2.33	2.18	1.54	1.68	0.0339	7.58
Na⁺*	252	0.491	0.379	0.368	0.442	0.079	4.48
K⁺*	244	0.123	0.0877	0.0973	0.102	0.00475	0.799
Mg²⁺*	155	0.117	0.0597	0.0778	0.128	0.00276	0.865
Ca²⁺*	246	0.839	0.503	0.586	1.35	0.141	14.7
TC*	166	11.8	9.71	9.54	7.3	0.16	36.5
OC*	166	10.1	8.08	8.23	6.43	0.29	32.4
EC*	166	1.79	1.61	1.46	1.04	0.07	5.64
PM_{2.5}*	253	16.8	14.0	12.6	14.8	0.468	124

*indicates that the parameters unit is µg.m⁻³.

In PM_{2.5-10}, the most observed elements were Ti, Th, Ca, Na, Mg, Al, Y, Nd (Table 4.2). Calcium, Al, Fe, Na, Mg, and K had the highest arithmetic mean concentrations. Calcium, Al, and Fe had also the highest geometric mean, respectively. Aluminium had the highest standard deviation. The most frequently observed anion and cation were Na⁺ and Cl⁻. Sulfate and Ca²⁺ had the highest arithmetic mean and geometric mean. OC concentrations were higher than EC concentrations.

Table 4.2. Statistical evaluation of measured parameter in PM_{2.5-10} (ng.m⁻³)

	N	Aritmetic mean	Median	Geometric mean	Standard deviation	Min	Max
Li	230	0.295	0.204	0.185	0.319	0.00106	2.56
Be	33	0.0257	0.0211	0.0186	0.0181	0.00265	0.0720
Na	262	307	261	254	494	3.46	8036
Mg	262	276	256	249	127	13.5	1151
Al	262	990	811	839	1192	66.9	15391
K	247	100	75.9	64.1	105	0.979	807
Ca	263	1088	827	779	948	8.92	6537
Sc	259	0.815	0.536	0.578	1.33	0.0470	16.6
Ti	265	23.8	18.0	17.2	25.4	0.209	242
V	258	1.51	0.631	0.565	4.80	0.00566	39.7
Cr	257	27.4	27.2	22.1	15.4	0.615	112
Mn	261	6.33	5.09	4.03	6.10	0.176	57.1
Fe	257	382	300	279	444	4.20	5792
Co	259	0.307	0.219	0.200	0.284	0.000872	1.92
Ni	249	5.09	2.88	2.57	6.03	0.0113	42.7
Cu	254	4.14	2.19	2.09	16.9	0.0429	265
Zn	255	12.1	7.25	7.65	16.8	0.673	156
Ge	161	0.0470	0.0349	0.0322	0.0448	0.00169	0.255
As	242	0.714	0.194	0.204	2.16	0.00248	14.7
Se	109	0.367	0.219	0.206	0.492	0.00565	2.89
Rb	262	0.389	0.292	0.252	0.405	0.0100	3.22
Sr	263	2.55	1.87	1.68	2.71	0.0219	21.4
Y	262	0.102	0.0706	0.0640	0.124	0.00310	1.01
Mo	230	0.262	0.192	0.165	0.268	0.00177	2.16
Cd	204	0.0643	0.0277	0.0257	0.0980	0.0000377	0.670
Sn	254	0.340	0.214	0.202	0.444	0.00597	4.10
Sb	256	0.251	0.217	0.187	0.172	0.00234	0.855
Cs	260	0.0357	0.0259	0.0253	0.0323	0.00144	0.234
Ba	261	9.08	6.25	5.87	19.6	0.0173	306
La	260	0.231	0.135	0.129	0.287	0.00220	1.84
Ce	260	0.508	0.274	0.268	0.662	0.00179	4.12
Pr	259	0.0449	0.0281	0.0264	0.0551	0.00150	0.433
Nd	262	0.135	0.0925	0.0803	0.183	0.00370	1.67
Sm	255	0.0229	0.0159	0.0137	0.0300	0.000242	0.264
Eu	225	0.00694	0.00485	0.00478	0.00791	0.000228	0.0606
Gd	255	0.0279	0.0191	0.0177	0.0330	0.000466	0.255
Tb	105	0.00458	0.00360	0.00323	0.00459	0.000801	0.0274
Dy	260	0.0189	0.0135	0.0120	0.0233	0.000935	0.194
Ho	118	0.00525	0.00368	0.00375	0.00572	0.000959	0.0386
Er	244	0.0117	0.00823	0.00721	0.0147	0.000116	0.121
Tm	39	0.00354	0.00211	0.00253	0.00337	0.000580	0.0162
Yb	240	0.0109	0.00683	0.00692	0.0148	0.000616	0.151

Table 4.2. Statistical evaluation of measured parameter in PM_{2.5-10} (ng.m⁻³) (continued)

	N	Aritmetic mean	Median	Geometric mean	Standard deviation	Min	Max
Lu	40	0.00336	0.00219	0.00244	0.00306	0.000307	0.0162
Hf	256	0.0367	0.0177	0.0172	0.208	0.00118	3.32
W	205	0.121	0.0653	0.0656	0.190	0.00116	1.81
Hg	187	0.0290	0.0201	0.0161	0.0326	0.0000161	0.285
Tl	191	0.0113	0.00710	0.00627	0.0157	0.0000882	0.147
Pb	253	1.97	1.12	0.986	4.00	0.0171	45.5
Bi	193	0.0186	0.0131	0.0118	0.0219	0.0000863	0.170
Th	265	0.0423	0.0309	0.0275	0.0505	0.000281	0.381
U	257	0.0186	0.0142	0.0125	0.0194	0.000676	0.175
Cl^{-*}	256	1.90	1.37	1.59	1.33	0.127	10.2
NO₃^{-*}	247	1.00	0.678	0.535	1.05	0.0137	7.82
SO₄^{2-*}	227	1.06	0.777	0.602	1.28	0.0146	9.87
NH₄⁺*	120	0.929	0.362	0.362	1.26	0.00370	6.48
Na⁺*	262	0.355	0.282	0.260	0.273	0.00122	1.85
K⁺*	219	0.0742	0.0608	0.0602	0.0653	0.00912	0.53
Mg²⁺*	200	0.0941	0.0537	0.0604	0.117	0.00611	0.82
Ca²⁺*	260	1.19	0.869	0.834	1.29	0.0301	12.0
TC*	172	14.3	11.9	11.6	9.33	2.76	45.8
OC*	172	12.2	10.8	9.8	8.22	2.24	42.0
EC *	172	2.12	1.94	1.77	1.26	0.21	6.94
PM_{2.5-10}	265	11.6	8.60	7.11	14.2	0.0387	113

*indicates that the parameters unit is µg.m⁻³.

4.2 Distribution characteristics of data

Frequency distributions are used to search about similarities and differences of environmental data. Generally, environmental data sets have high standard deviations because of the large variability of the atmospheric concentrations due mostly to meteorological conditions, physical and chemical changes, differences in sources and air mass transport patterns. In addition, the geometric mean and median values are close to each other as they show lognormal distribution (Yenisoy Karakaş, 2000).

A data matrix generally shows normally distributed values and was described by using arithmetic mean and standard deviation. This is a symmetric Gaussian

distribution. However, the data set affected by different pollution sources and therefore parameters generally follow a log-normal distribution in environmental studies (Karakaş, 1999).

Skewness, Kurtosis, DN value and p-values were calculated to determine the distribution type of the obtained data in PM_{2.5} and PM_{2.5-10} (Table 4.3. and Table 4.4.). Skewness is one of the important parameters to characterize the distribution types. It is used to measure the symmetry or shape of the data. If the skewness value is 0, the data is symmetrically distributed. It can be classified also left sided and right sided asymmetry. Kurtosis is also used to measure relative peakedness or flatness compared to a bell-shaped curve. If the standard skewness and standard kurtosis values are outside the range (-2.0) to (+2.0), the data matrix may show a normal distribution. (Yenisoy Karakaş, 2000). Kolmogorov-Smirnov D statistic calculates the maximum distance between the empirical cumulative distribution function and the fitted cumulative distribution function (Statgraph user manual, 2006) and used for testing lognormal distribution of data (Yenisoy Karakaş, 2000). The p value is the probability of finding the observed results when the null hypothesis (H₀) of a study question is true (Statgraph user manual, 2006).

In this study, Statgraphics Centurion XVII software was used to determine which distribution types fits the data by performing the Kolmogorov-Smirnov (KS-DN). Firstly, the data matrix was checked for distribution types (normal, lognormal or Weibull distribution). All the parameters were also checked standard skewness and standard kurtosis obtained by the Statgraphics Centurion XVII software. Then p-value and DN values was checked for the determination of distribution type. If the p-value was smaller than 0.05, the software was not able to determine the distribution types. In that case, the distribution type with the smallest DN value was selected.

As given in Table 4.3 and Table 4.4, the most of the elements was lognormally distributed. All measured parameters were positively skewed. Kurtosis value were positive except for NH₄⁺ in PM_{2.5}.

Lithium, Be, K, Ca, Mn, Rb, Sr, Mo, Cd, Sb, Hg, Tl, NO₃⁻, SO₄²⁻, and EC in PM_{2.5-10} and Fe, Rb, Cs, NO₃⁻, NH₄⁺ and EC in PM_{2.5} showed Weibull distributions. If a series of data shows weibull distribution, the species are affected from the local

sources. (Karaca et al., 2006). Magnesium, Cr, NH_4^+ , Na^+ in $\text{PM}_{2.5-10}$ and Be and Mg in $\text{PM}_{2.5}$ showed normal distribution. Generally, most of the parameters showed lognormal distribution in two types of particles. As said before, it is a general manner for environmental samples. Some examples of frequency histogram for two types of particles were illustrated in Figure 4.1 and 4.2.

Table 4.3. Distribution parameters of elements, ions and carbonaceous species in $\text{PM}_{2.5-10}$

Parameters	Skewness	Kurtosis	DN value	P-value	Distribution type
Li	3.31	15.7	0.0673	0.250	Weibull
Be	0.771	0.208	0.122	0.706	Weibull
Na	14.8	232	0.160	0.00	Lognormal
Mg	2.77	14.1	0.161	0.00	Normal
Al	9.79	107	0.137	0.00	Lognormal
K	3.25	15.1	0.0850	0.0565	Weibull
Ca	2.48	8.75	0.0735	0.117	Weibull
Sc	8.18	84.1	0.1149	0.0021	Lognormal
Ti	4.40	27.5	0.064	0.230	Lognormal
V	6.37	41.0	0.0960	0.017	Lognormal
Cr	1.16	4.49	0.076	0.101	Normal
Mn	3.24	20.0	0.0402	0.793	Weibull
Fe	8.06	89.6	0.098	0.0149	Lognormal
Co	1.99	6.07	0.0458	0.648	Lognormal
Ni	2.45	8.44	0.0474	0.631	Lognormal
Cu	14.7	225	0.0524	0.500	Lognormal
Zn	5.27	35.3	0.0506	0.548	Lognormal
Ge	3.80	23.0	0.0447	0.904	Lognormal
As	4.87	23.5	0.0897	0.0407	Lognormal
Se	3.01	9.73	0.088	0.366	Lognormal
Rb	3.25	15.5	0.0584	0.335	Weibull
Sr	3.51	16.9	0.0707	0.145	Weibull
Y	3.87	19.6	0.076	0.0947	Weibull
Mo	3.26	18.1	0.0448	0.745	Weibull
Cd	3.29	13.1	0.0498	0.691	Weibull
Sn	4.11	24.5	0.0590	0.343	Lognormal
Sb	1.10	1.37	0.0278	0.989	Lognormal
Cs	2.40	8.43	0.0604	0.301	Lognormal
Ba	13.6	205	0.0830	0.055	Lognormal
La	2.83	9.63	0.057	0.36	Lognormal
Ce	2.77	9.00	0.048	0.58	Lognormal

Table 4.3 Distribution parameters of elements, ions and carbonaceous species in PM_{2.5-10} (continued)

Parameter s	Skewness	Kurtosis	DN value	P-value	Distribution type
Pr	3.22	13.8	0.062	0.27	Lognormal
Nd	4.41	25.8	0.079	0.0009	Lognormal
Sm	4.32	24.5	0.083	0.0588	Lognormal
Eu	3.82	18.3	0.090	0.05	Lognormal
Gd	3.66	17.3	0.063	0.2570	Lognormal
Tb	2.50	7.44	0.084	0.46	Lognormal
Dy	3.90	19.9	0.061	0.29	Lognormal
Ho	3.31	13.4	0.080	0.446	Lognormal
Er	4.26	24.0	0.079	0.092	Lognormal
Tm	2.04	4.67	0.150	0.351	Lognormal
Yb	5.43	40.8	0.068	0.222	Lognormal
Lu	2.31	7.10	0.091	0.898	Lognormal
Hf	15.6	248	0.081	0.067	Lognormal
W	5.30	37.3	0.084	0.113	Lognormal
Hg	3.63	21.6	0.059	0.546	Weibull
Tl	4.80	32.9	0.073	0.259	Weibull
Pb	7.06	63.7	0.065	0.230	Lognormal
Bi	4.14	22.5	0.083	0.143	Lognormal
Th	3.91	19.2	0.065	0.206	Lognormal
U	3.69	20.9	0.071	0.149	Weibull
Cl⁻	2.26	7.24	0.139	0.000	Lognormal
NO₃⁻	2.18	8.66	0.0662	0.230	Weibull
SO₄²⁻	3.43	16.0	0.0588	0.419	Weibull
NH₄⁺	2.07	4.30	0.254	3.80x10 ⁻⁷	Normal
Na⁺	1.48	3.27	0.142	5.16x10 ⁻⁵	Normal
K⁺	3.94	19.7	0.100	0.024	Lognormal
Mg²⁺	3.50	15.4	0.126	0.003	Lognormal
Ca²⁺	4.12	24.4	0.0533	0.460	Lognormal
TC	1.19	1.18	0.0511	0.761	Lognormal
OC	1.29	1.57	0.0625	0.527	Lognormal
EC	1.12	1.52	0.0579	0.611	Weibull

Table 4.4. Distribution parameters of elements, ions and carbonaceous species in PM_{2.5}

	Skewness	Kurtosis	DN value	P-value	Distribution type
Li	4.32	25.0	0.0449	0.748	Lognormal
Be	0.217	0.0856	0.0686	0.975	Normal
Na	10.7	126	0.232	0.00	Lognormal
Mg	8.93	95.5	0.286	0.00	Normal
Al	5.76	43.3	0.234	0.00	Lognormal
K	11.4	152	0.0818	0.0725	Lognormal
Ca	7.22	69.8	0.0725	0.140	Lognormal
Sc	5.93	40.4	0.0859	0.0477	Lognormal
Ti	3.79	17.7	0.128	0.0005	Lognormal
V	9.11	90.7	0.0748	0.119	Lognormal
Cr	9.50	107	0.125	0.0007	Lognormal
Mn	7.55	69.3	0.0704	0.165	Lognormal
Fe	8.67	103	0.136	0.0003	Weibull
Co	5.32	38.0	0.0367	0.888	Lognormal
Ni	7.29	66.0	0.0386	0.852	Lognormal
Cu	6.22	54.7	0.0762	0.110	Lognormal
Zn	4.26	26.9	0.0559	0.413	Lognormal
Ge	3.80	23.0	0.0648	0.417	Lognormal
As	6.29	52.0	0.0830	0.0614	Lognormal
Se	2.98	10.4	0.106	0.0210	Lognormal
Rb	13.8	205	0.0827	0.0630	Weibull
Sr	12.7	183	0.0938	0.0245	Lognormal
Y	5.78	38.7	0.144	0.0000705	Lognormal
Mo	6.13	48.8	0.0409	0.845	Lognormal
Cd	5.00	43.0	0.0647	0.271	Lognormal
Sn	2.15	6.8	0.0346	0.925	Lognormal
Sb	6.45	66.0	0.0851	0.0518	Lognormal
Cs	4.74	38.9	0.0682	0.192	Weibull
Ba	15.9	252	0.0643	0.248	Lognormal
La	5.70	50.3	0.145	0.00	Lognormal
Ce	6.40	61.9	0.181	0.00	Lognormal
Pr	3.82	19.5	0.158	0.00	Lognormal
Nd	4.31	20.1	0.124	0.0009	Lognormal
Sm	4.42	21.7	0.125	0.0014	Lognormal
Eu	12.5	157	0.199	0.00	Lognormal
Gd	14.7	217	0.118	0.0038	Lognormal
Tb	3.32	12.3	0.272	0.00	Lognormal
Dy	4.77	25.2	0.166	0.00	Lognormal

Table 4.4. Distribution parameters of elements, ions and carbonaceous species in PM_{2.5} (continued)

	Skewness	Kurtosis	DN value	P-value	Distribution type
Ho	3.97	17.5	0.250	0.00	Lognormal
Er	7.29	66.2	0.266	0.00	Lognormal
Tm	3.15	11.2	0.235	0.0419	Lognormal
Yb	8.07	76.9	0.242	0.00	Lognormal
Lu	3.81	16.0	0.205	0.0897	Lognormal
Hf	11.6	141	0.147	0.00	Lognormal
W	6.04	41.7	0.05	0.658	Lognormal
Hg	8.40	92.6	0.104	0.0191	Lognormal
Tl	5.51	40.4	0.0318	0.977	Lognormal
Pb	8.61	97.1	0.0935	0.0240	Lognormal
Bi	3.25	14.7	0.0535	0.540	Lognormal
Th	6.22	44.7	0.179	0.00	Lognormal
U	6.22	49.3	0.0827	0.07	Lognormal
Cl⁻	1.94	4.95	0.163	0.00	Lognormal
NO₃⁻	2.73	15.4	0.0740	0.138	Weibull
SO₄²⁻	2.12	4.35	0.0678	0.267	Lognormal
NH₄⁺	0.59	-0.27	0.0914	0.0472	Weibull
Na⁺	3.78	26.9	0.0491	0.578	Lognormal
K⁺	2.87	12.4	0.0731	0.148	Lognormal
Mg²⁺	3.00	12.1	0.145	0.00294	Lognormal
Ca²⁺	7.28	63.1	0.125	0.000957	Lognormal
TC	1.09	0.928	0.0694	0.406	Lognormal
OC	1.15	1.01	0.0471	0.855	Lognormal
EC	0.978	1.28	0.0586	0.618	Weibull

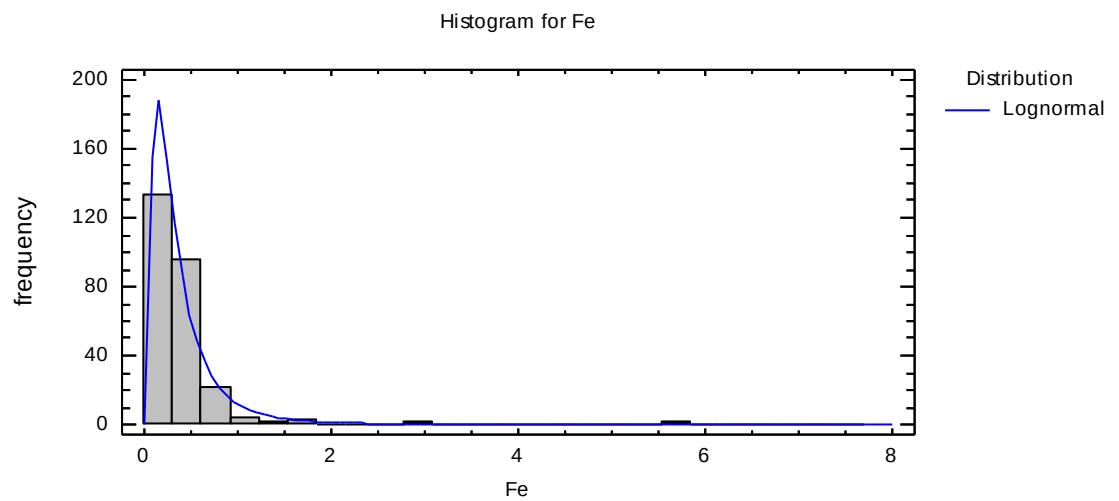
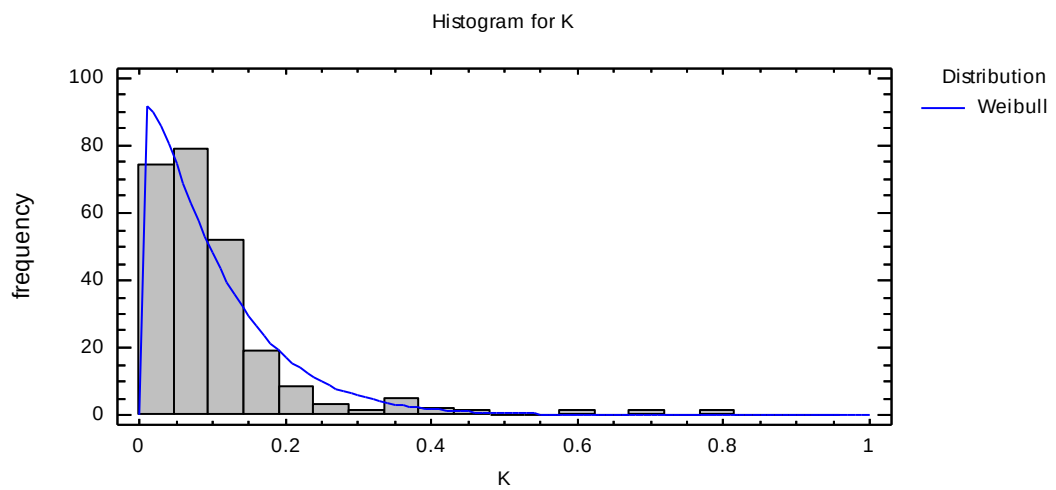
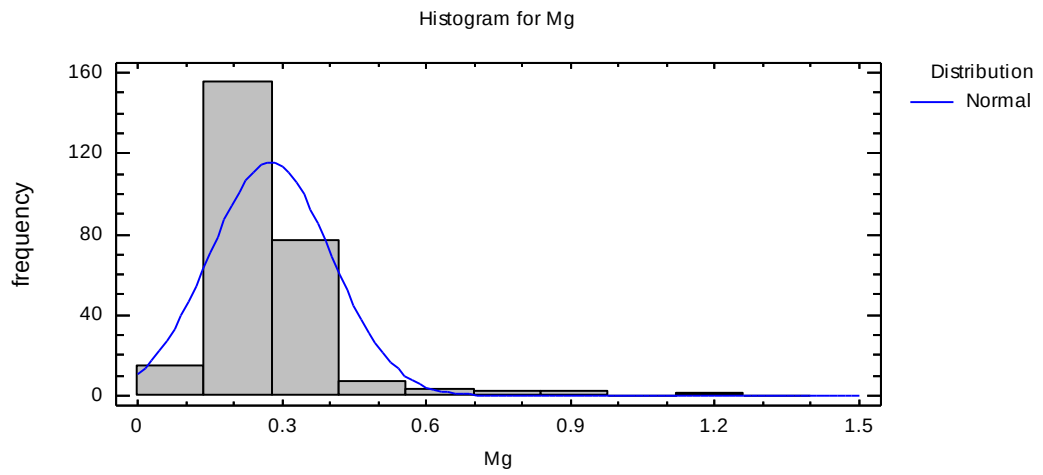


Figure 4.1. Some examples of frequency histogram for $PM_{2.5-10}$

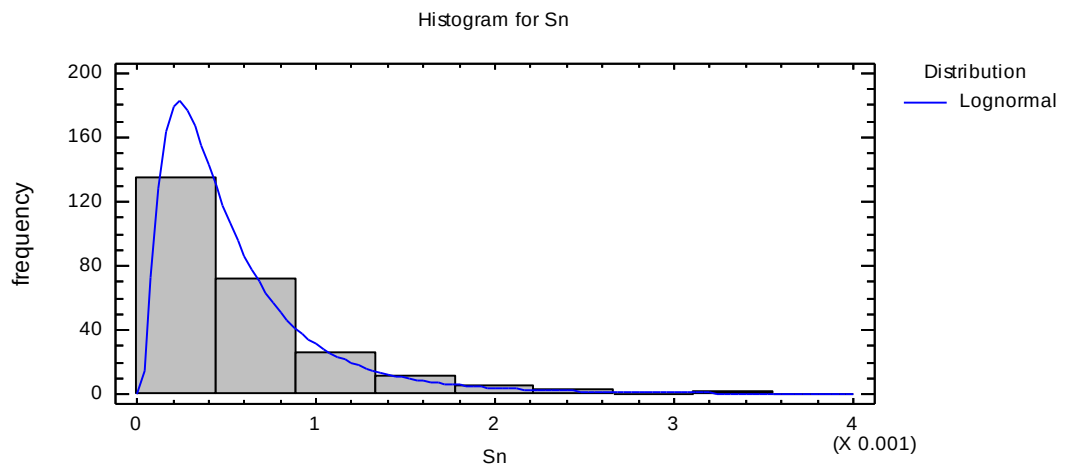
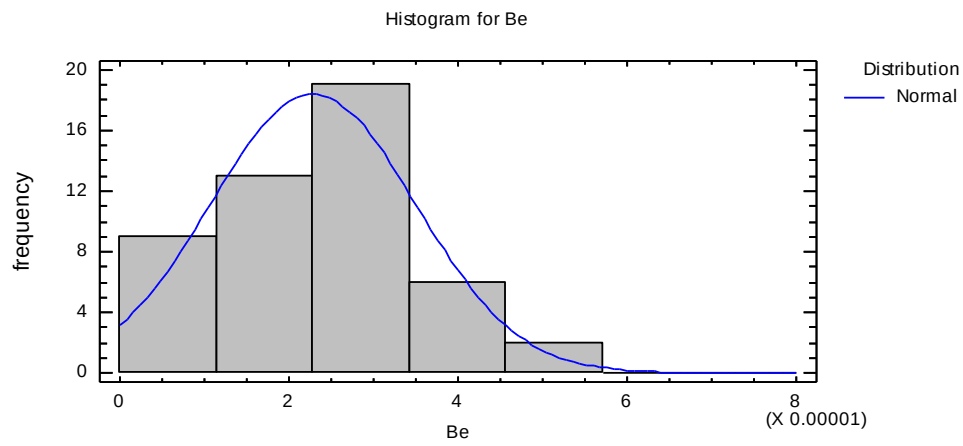


Figure 4.2. Some examples of frequency histogram for $PM_{2.5}$

4.3 Concentrations of particulate matter

The temporal variations of $PM_{2.5}$ and $PM_{2.5-10}$ concentrations were illustrated in Figure 4.3. There were some coincident peaks in two types of particles.

Generally, $PM_{2.5-10}$ concentrations were higher than $PM_{2.5}$ concentrations in whole year. The highest concentration was observed in May for $PM_{2.5}$ and in December for $PM_{2.5-10}$.

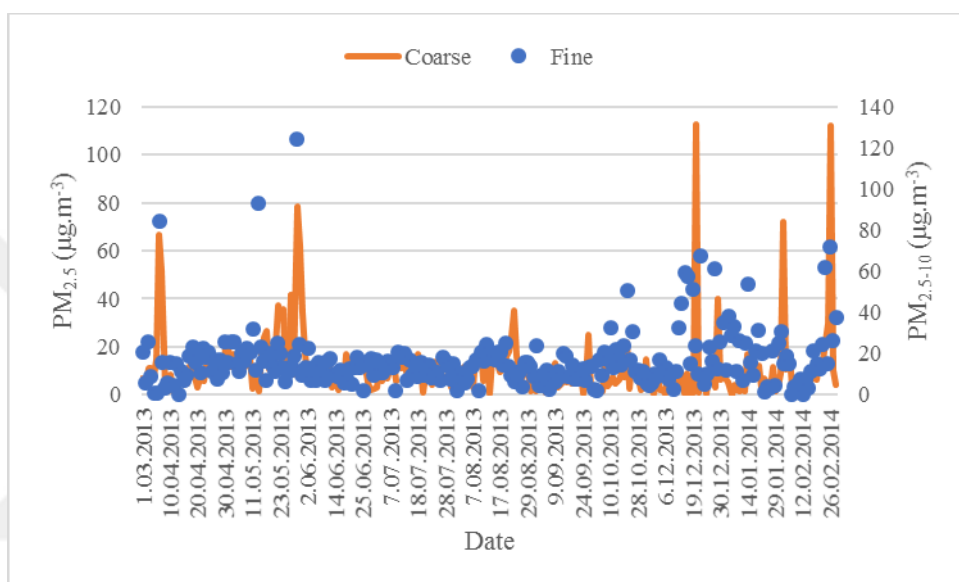


Figure 4.3. The temporal variations of $PM_{2.5}$ and $PM_{2.5-10}$

$PM_{2.5-10}/PM_{2.5}$ ratio gives a general clue of sources of pollutants. If the ratio is greater than one, local sources are more effective. Median values are used to obtain the ratio. Because arithmetic mean values can be affected from outlier values in a data set. Figure 4.4 shows $PM_{2.5-10}/PM_{2.5}$ ratios of median values of elements, ions and carbonaceous species. The ratios are changing from 3.6 to 0.17. Crustal elements, such as Er, Sm, Y, Nd, Yb, Dy, Pr, Sr, Gd, Ho, Tb, Ce, La, Th, Ca, Fe, Eu, U, Lu, Be and EC/OC were mostly found in the coarse fraction. Anthropogenic species like As, Se, Zn, Pb, Cd, Sb, Sn, Cs, W, Hg, Tl were mostly in the fine fraction.

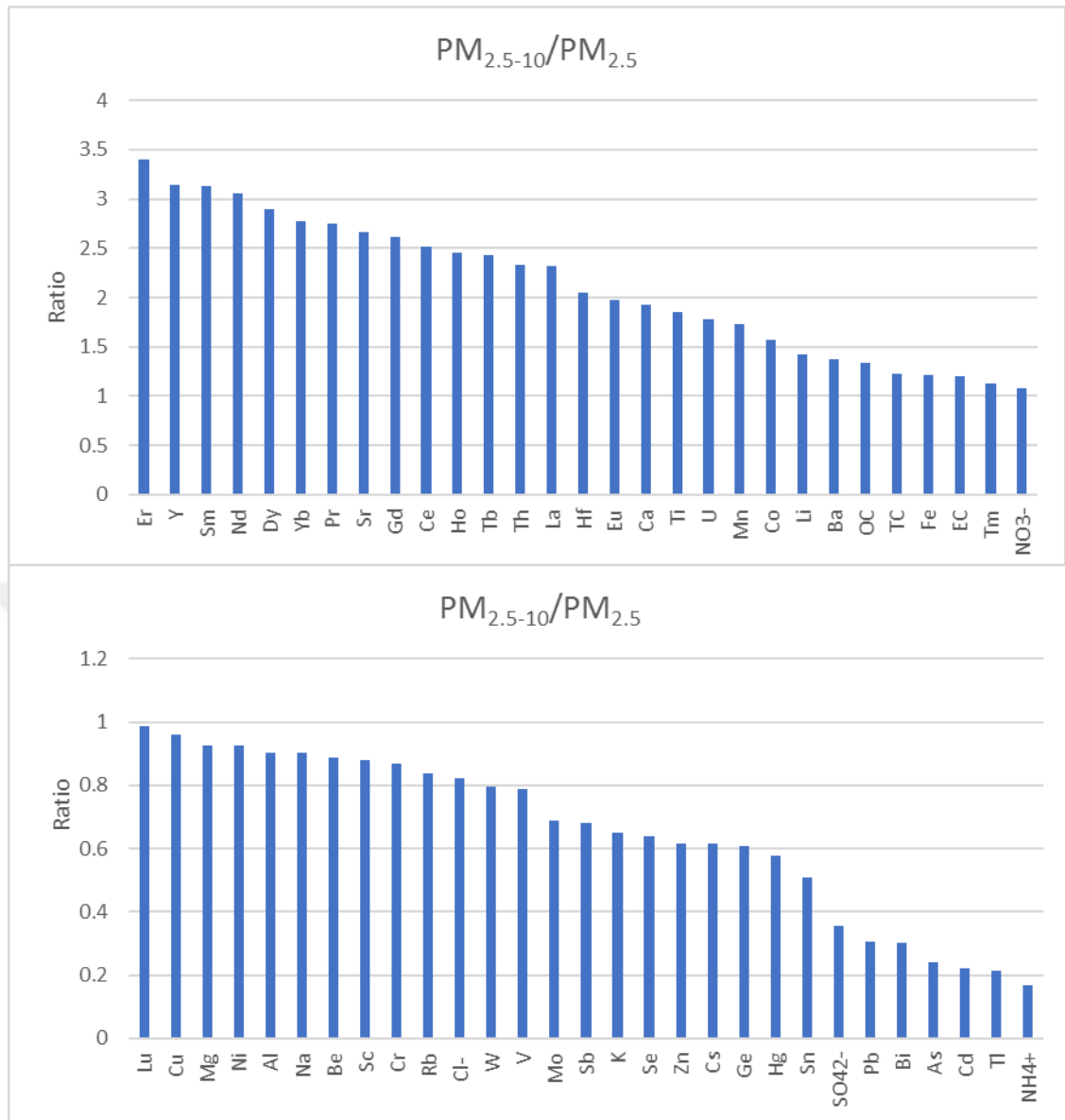


Figure 4.4. Coarse to fine ratios of median values of elements, ions, and carbonaceous species

Figure 4.5 shows monthly mean variations for $PM_{2.5}$ and PM_{10} concentrations in the sampling period. PM_{10} concentrations were the sum of $PM_{2.5}$ and $PM_{10-2.5}$ concentrations. Weather condition of Bolu is similar with Black Sea Region and there is an almost continuous need of heating process. In summer, heating process occurs especially at higher altitudes of Bolu Mountains, not in the city center. Therefore, the period between June-2013-September 2013 was selected as the nonheating season and period between March 2013- May 2013 and October 2013- February 2014 were named as the heating season. The arithmetic means and standard deviations for the nonheating season were lower than the heating season.

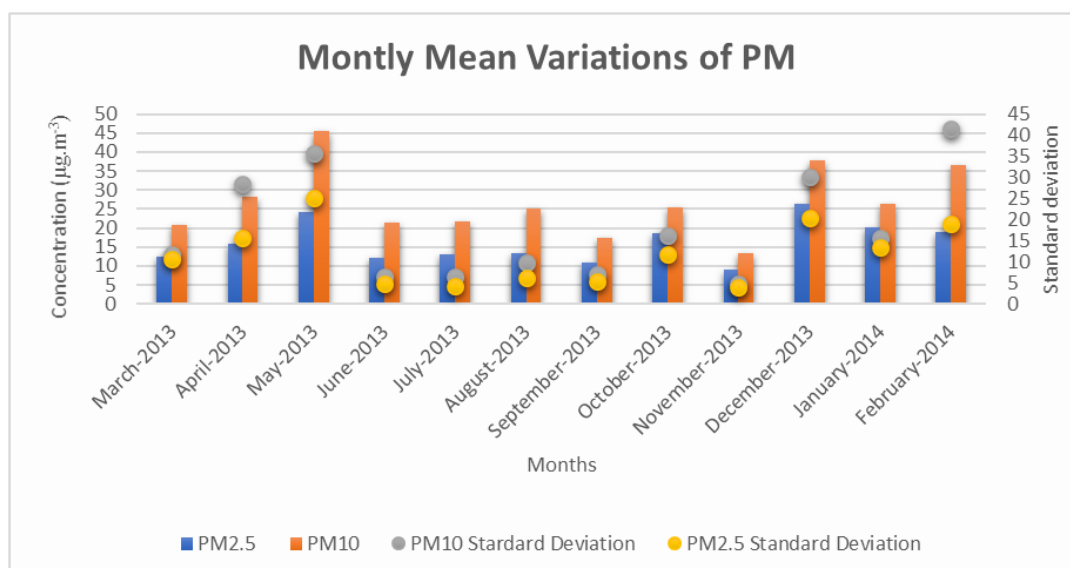


Figure 4.5. Montly mean variations of PM_{2.5} and PM₁₀

Compositions of the PMs are very complex because they can be affected by many sources (Valavanidis et al., 2008). Elements, ions, carbonaceous aerosols are the most known components of the PM. Therefore, PM_{2.5-10} and PM_{2.5} was investigated by using individual compositions of elements, ions, and carbonaceous aerosols in the sampling season.

4.4 Concentrations of elements

Daily concentration values of elements in PM_{2.5} and PM_{2.5-10} are shown in Figure 4.6 and 4.7. Variations for each element were shown separately for each date. Calcium, Al, Fe, Mg, Na, K were higher than other elements in PM_{2.5} and PM_{2.5-10} during the whole sampling period, respectively. Soil-originated elements like Sc, Eu, Sm, Dy, Lu, Nd, U, Th, Er, Ho, Yb, Tm, Gd, Y and antropojenic elements like As and V showed similar variation in PM_{2.5} and PM_{10-2.5}.



Figure 4.6. Temporal variations of trace metals in $\text{PM}_{2.5}$

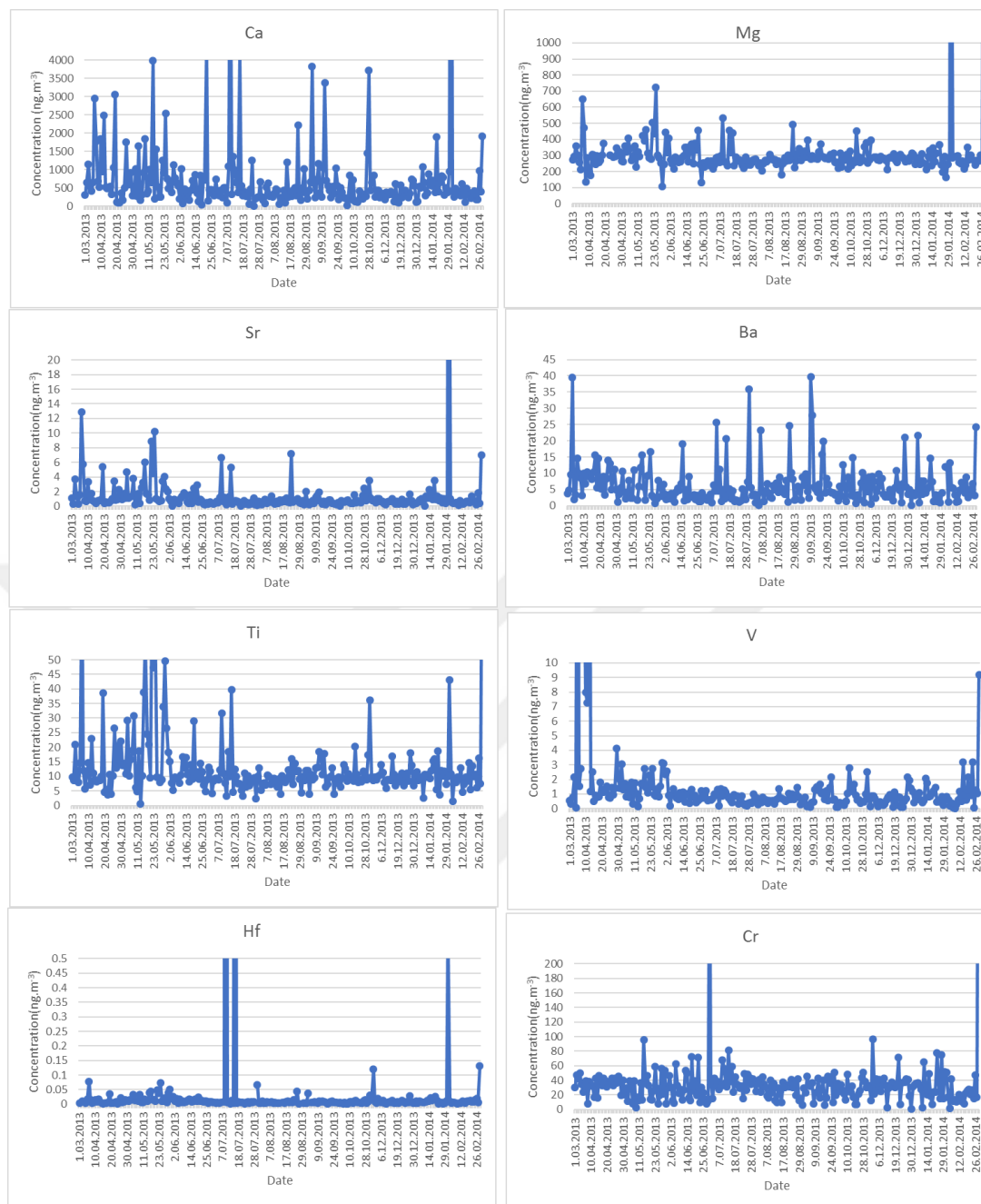


Figure 4.6. Temporal variations of trace metals in PM_{2.5} (continued)

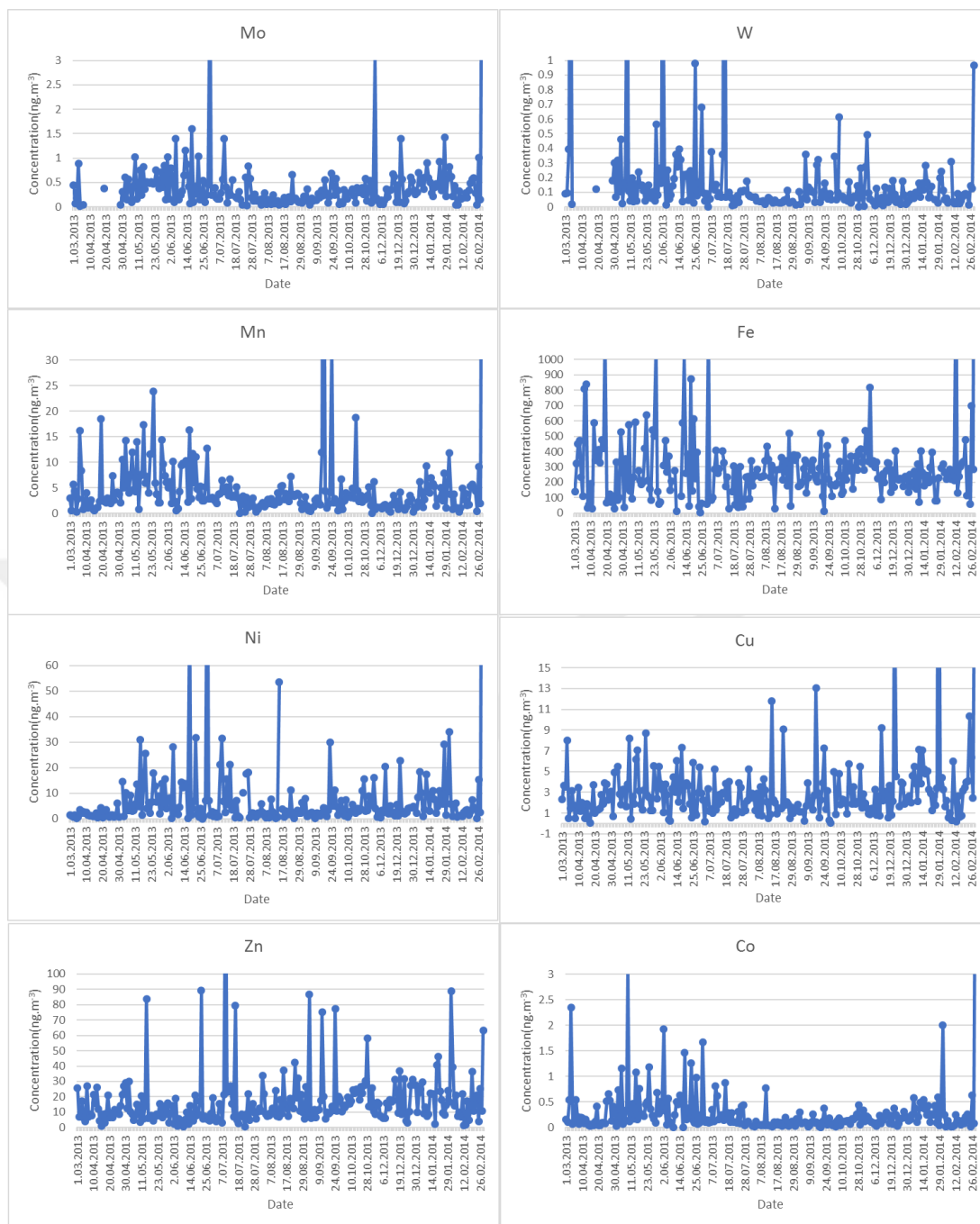


Figure 4.6. Temporal variations of trace metals in PM_{2.5} (continued)

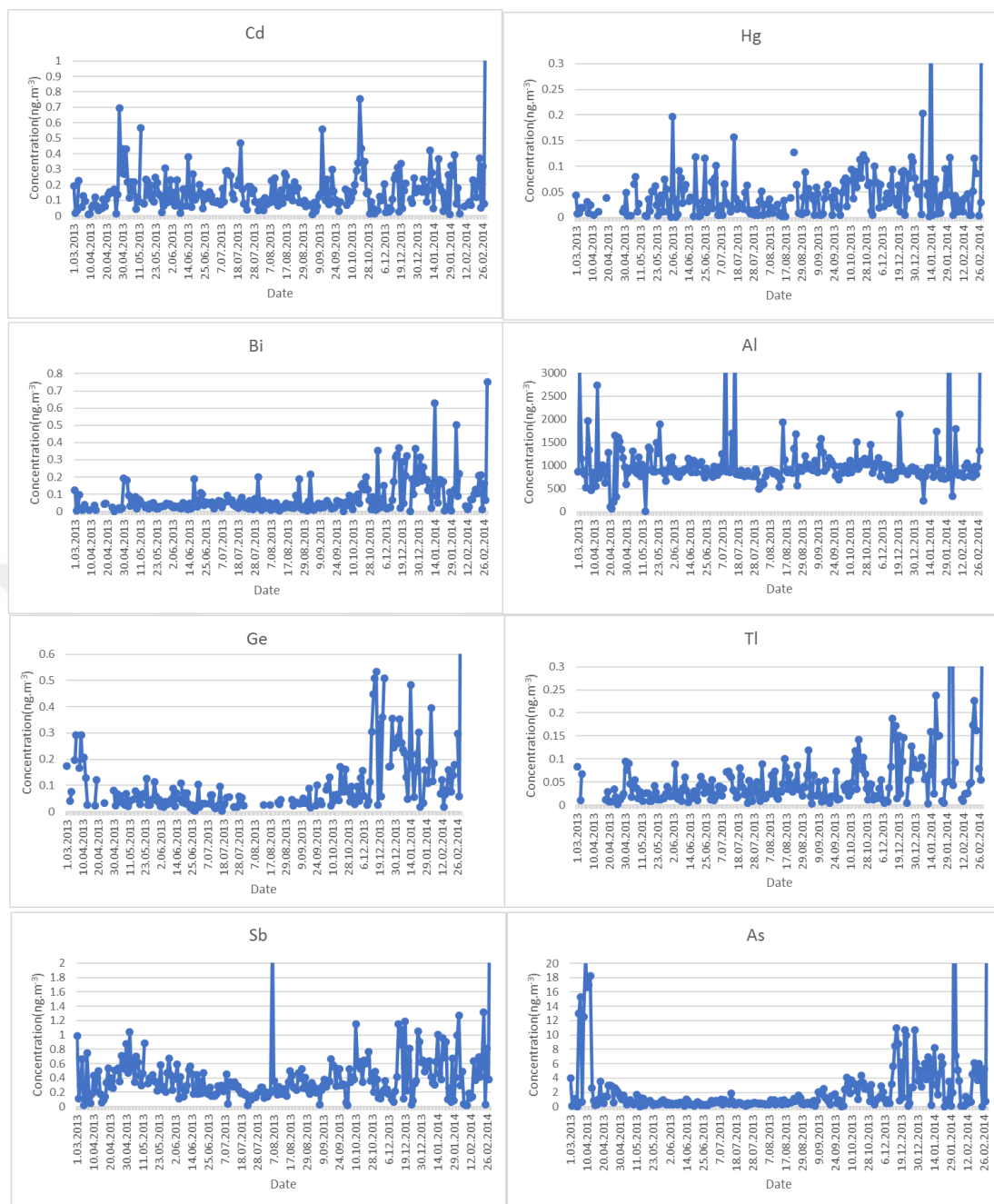


Figure 4.6. Temporal variations of trace metals in $PM_{2.5}$ (continued)



Figure 4.6. Temporal variations of trace metals in PM_{2.5} (continued)

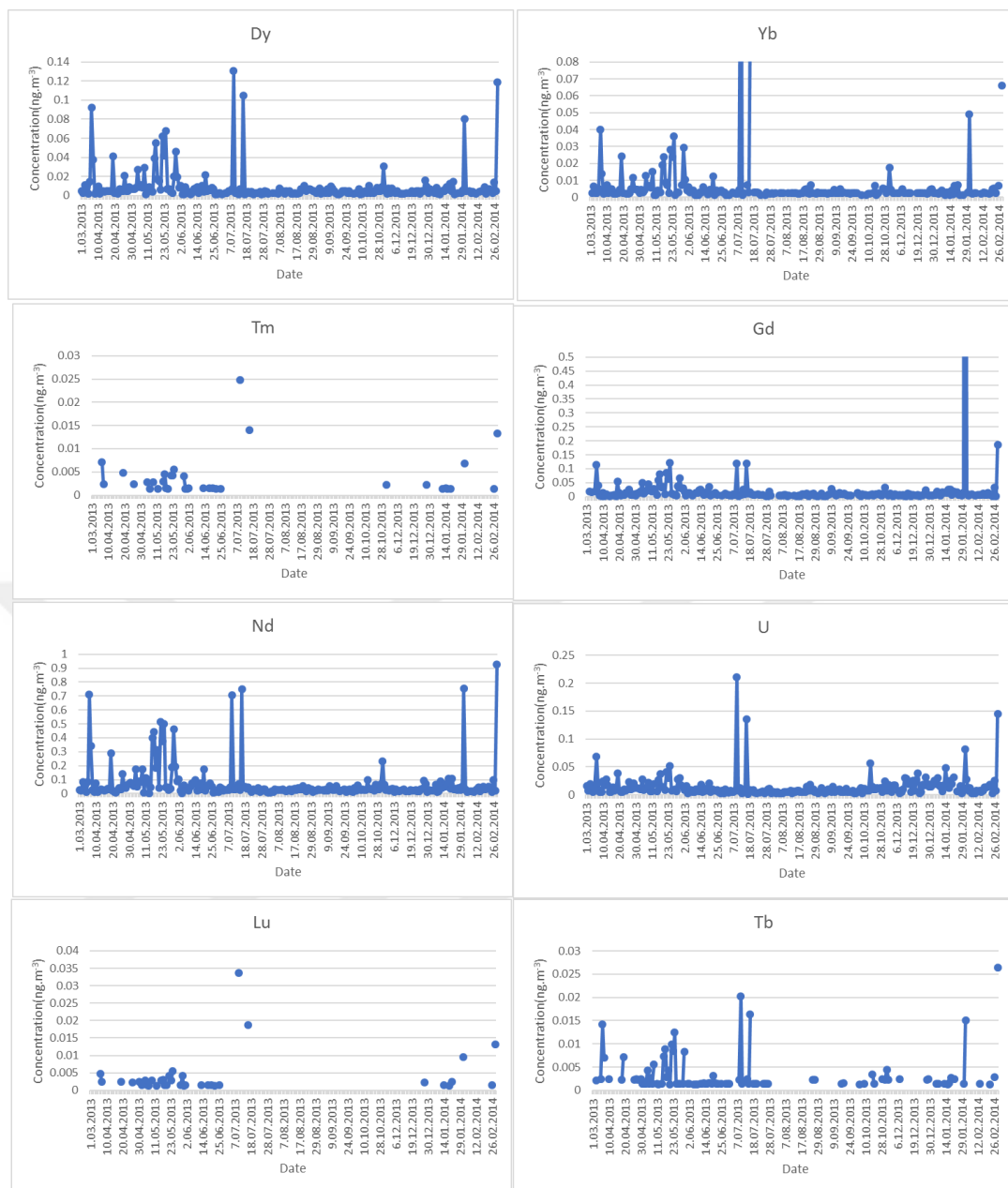


Figure 4.6. Temporal variations of trace metals in $PM_{2.5}$ (continued)

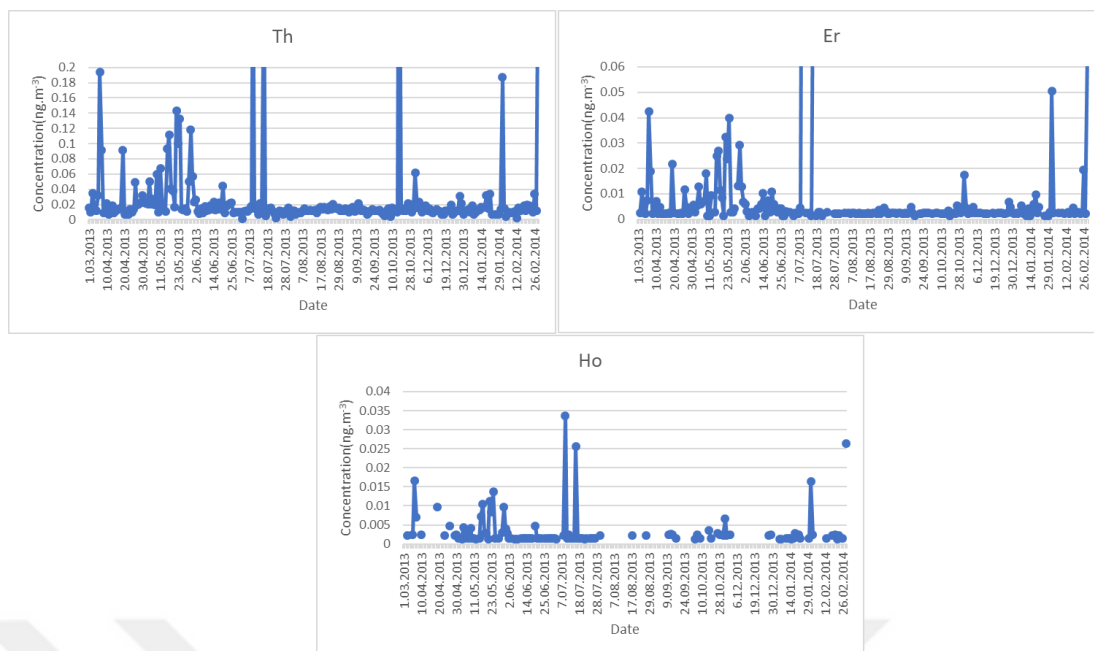


Figure 4.6. Temporal variations of trace metals in PM_{2.5} (continued)

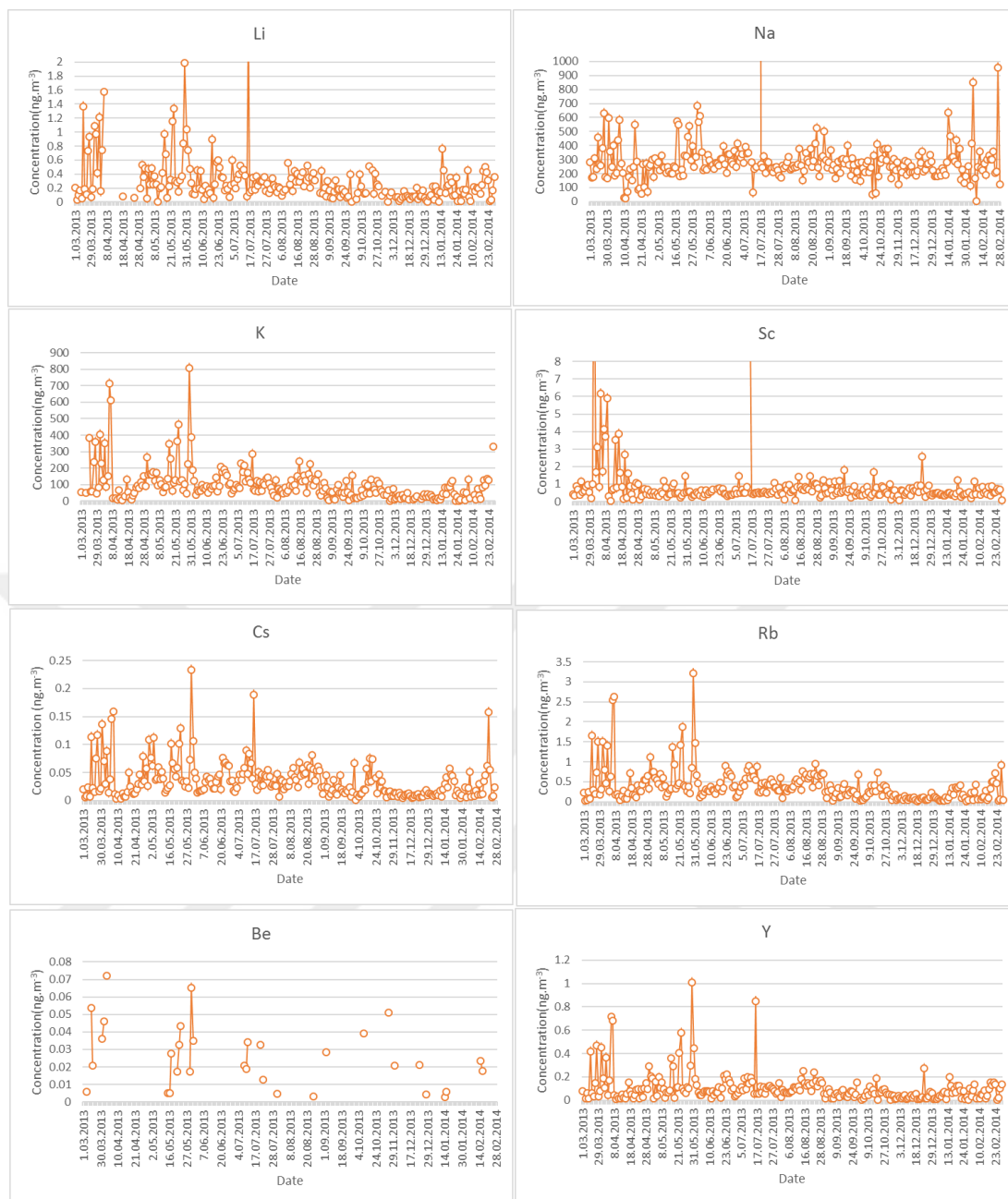


Figure 4.7. Temporal variations of elements in $PM_{2.5-10}$



Figure 4.7. Temporal variations of elements in $\text{PM}_{2.5-10}$ (continued)

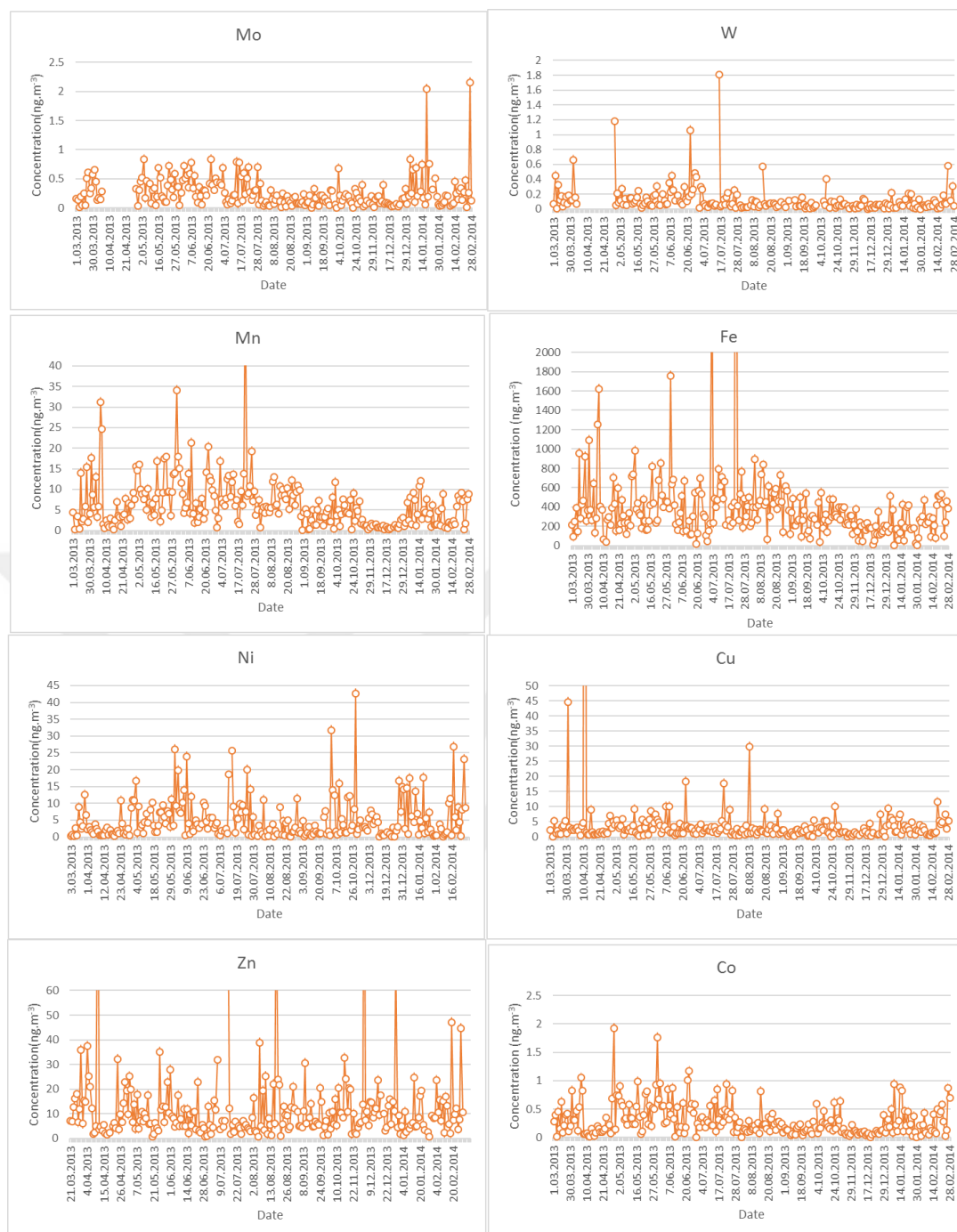


Figure 4.7. Temporal variations of elements in $PM_{2.5-10}$ (continued)

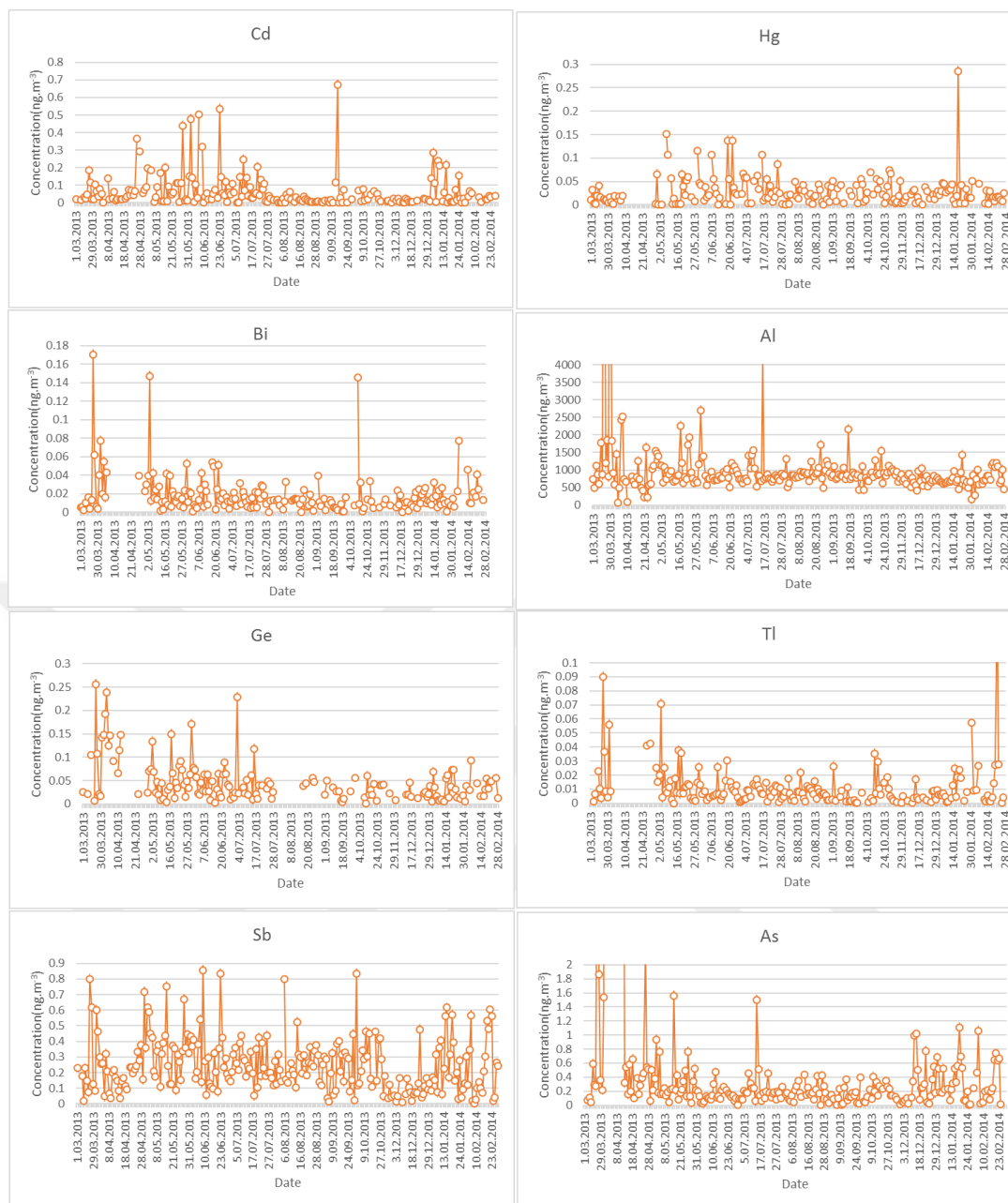


Figure 4.7. Temporal variations of elements in $\text{PM}_{2.5-10}$ (continued)

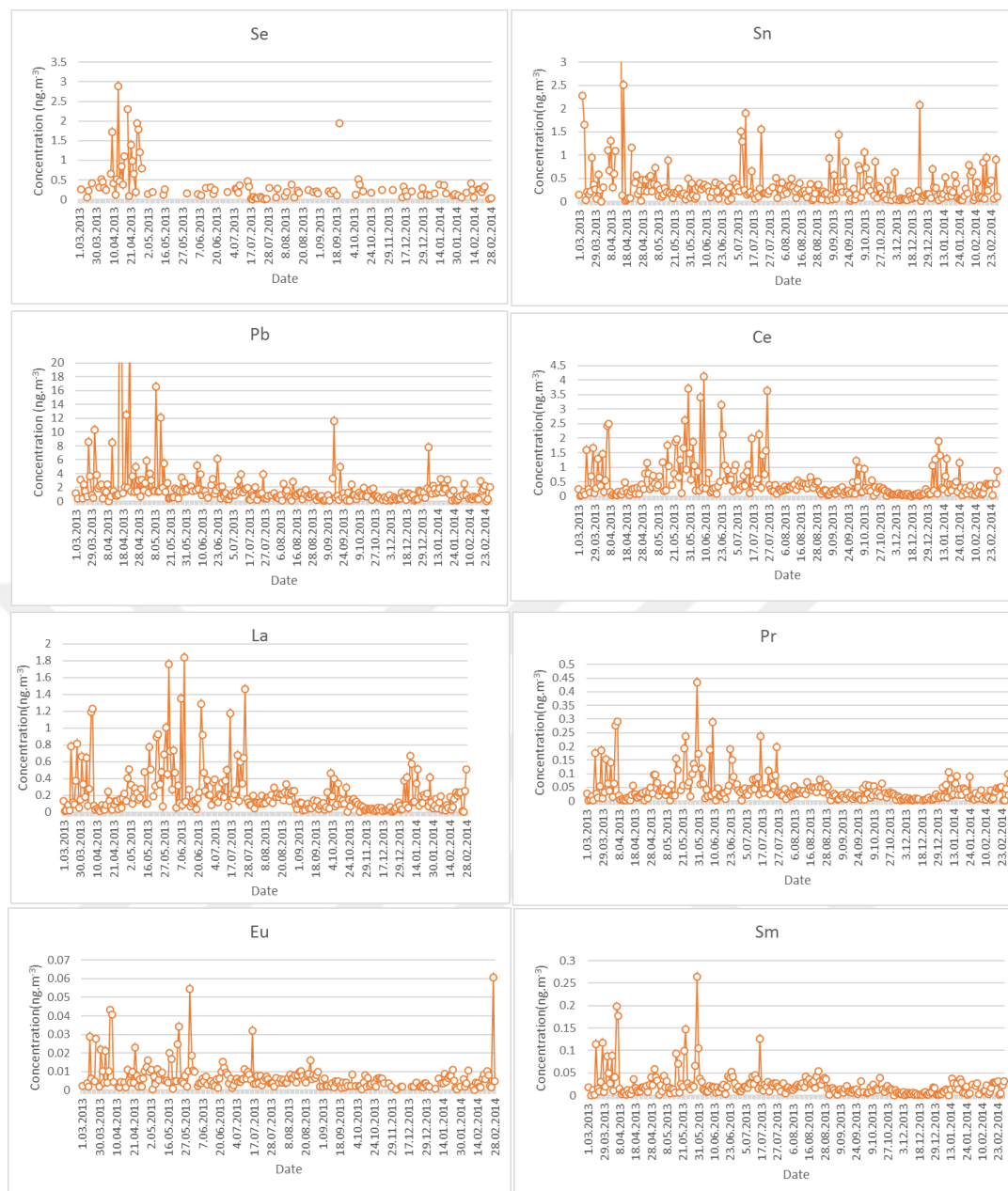


Figure 4.7. Temporal variations of elements in $\text{PM}_{2.5-10}$ (continued)

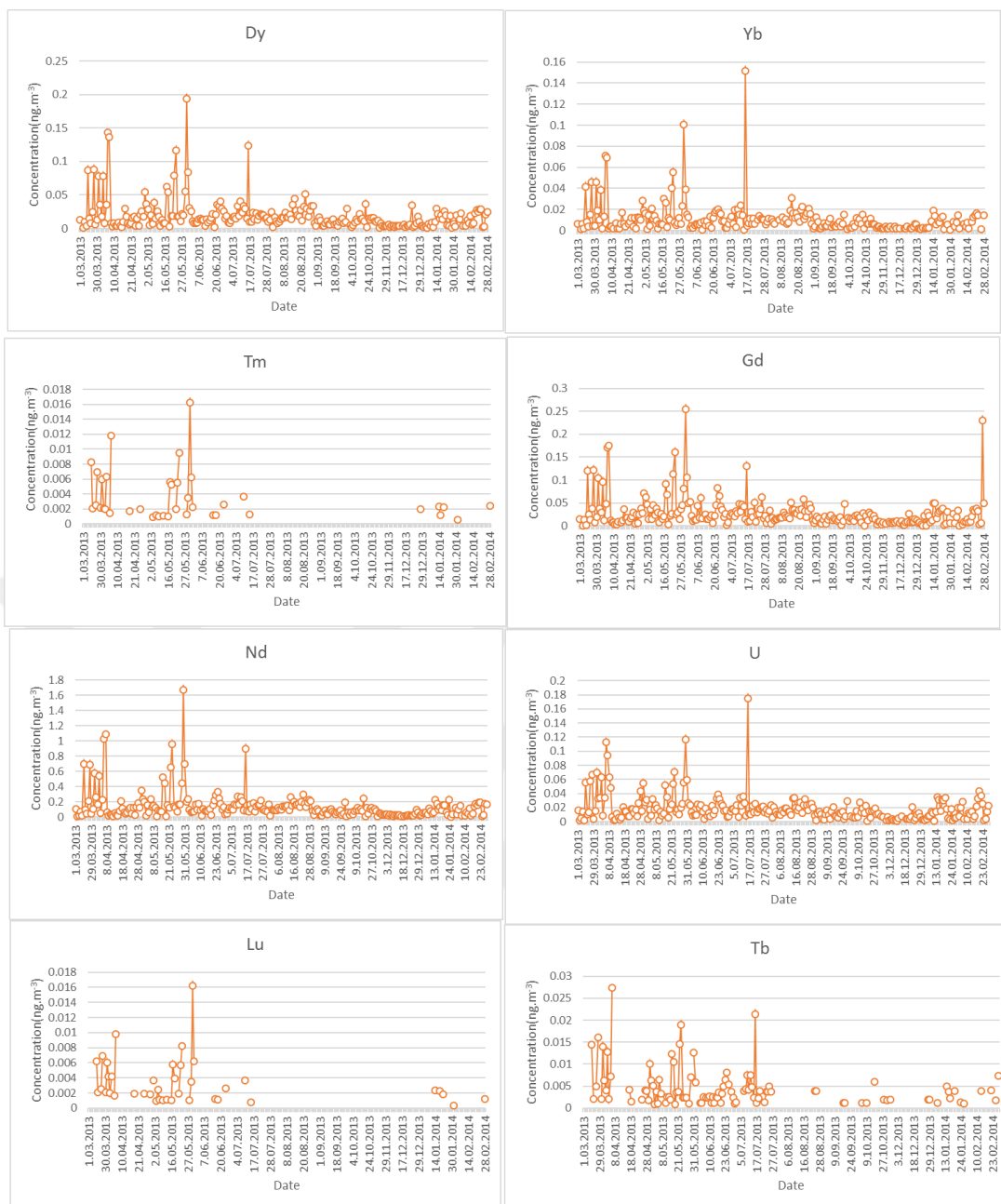


Figure 4.7. Temporal variations of elements in PM_{2.5-10} (continued)

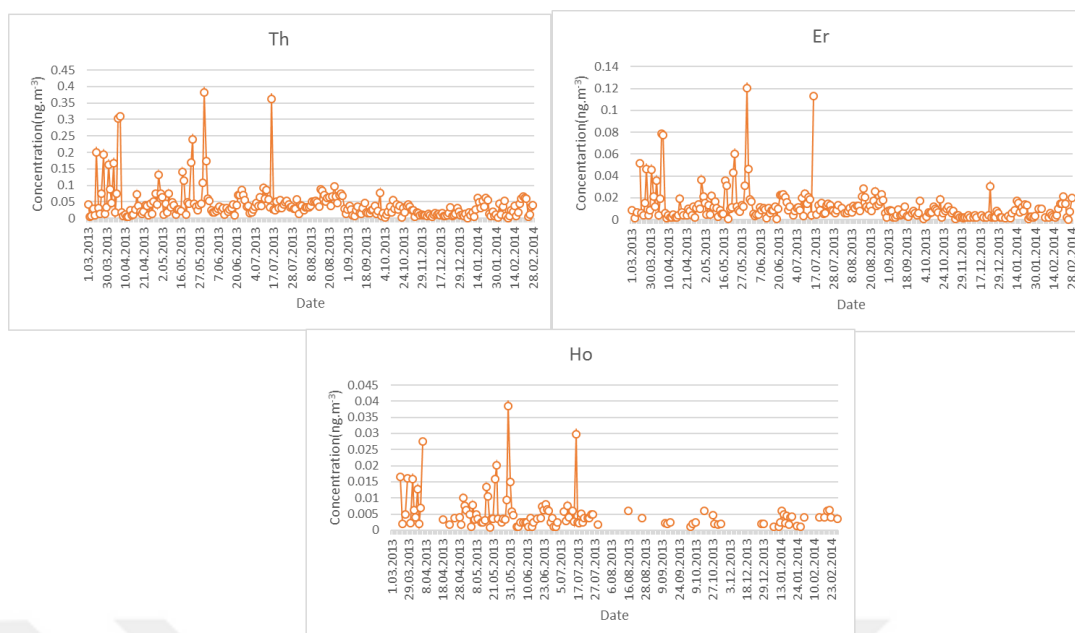


Figure 4.7. Temporal variations of elements in PM_{2.5-10} (continued)

4.5 Concentrations of ions

The concentrations of Cl^- , NO_2^- , NO_3^- , SO_4^{2-} anions and Na^+ , Ca^{2+} , Mg^{2+} , K^+ and NH_4^+ cations were determined. The values of F^- , NO_2^- , Br^- , PO_4^{2-} anions and Li^+ cations were below limit of detection. Figure 4.8 and 4.9 shows the temporal variations of ion concentrations.

Bolu is a city between the two metropolitan cities, İstanbul and Ankara, and the important highways connecting the cities (TEM and D100) is near the sampling site. In addition, the city is an important agricultural area for Turkey and there are lots of hen houses in the city. There is also usage of natural fertilizer in the farming areas. Therefore, there were continual sources of NH_4^+ and NO_3^- . That's why NH_4^+ concentrations were higher in spring and summer season in PM_{2.5-10} because of the high agricultural activity close to the sampling point.

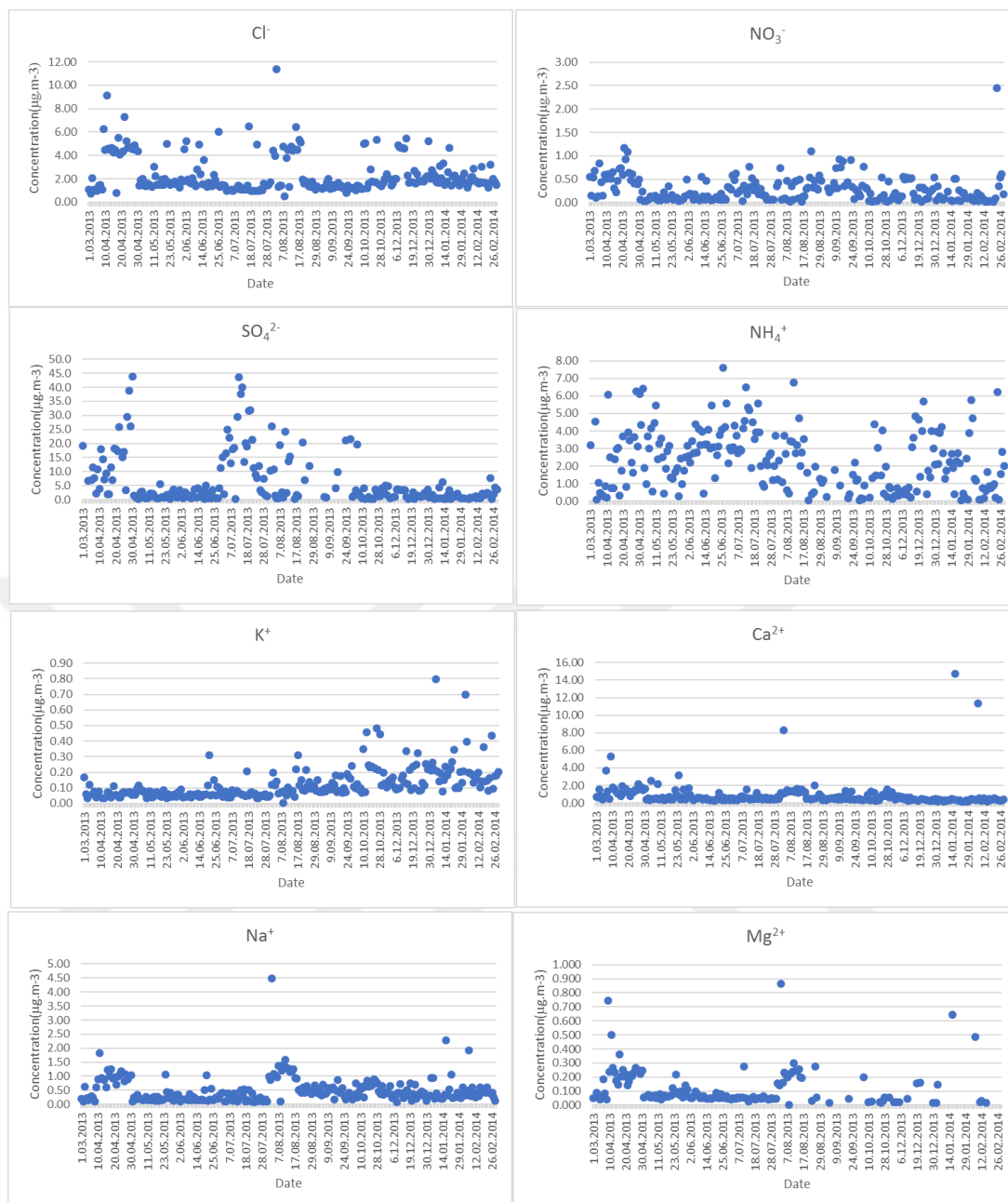


Figure 4.8. Temporal variations of ions in PM_{2.5}

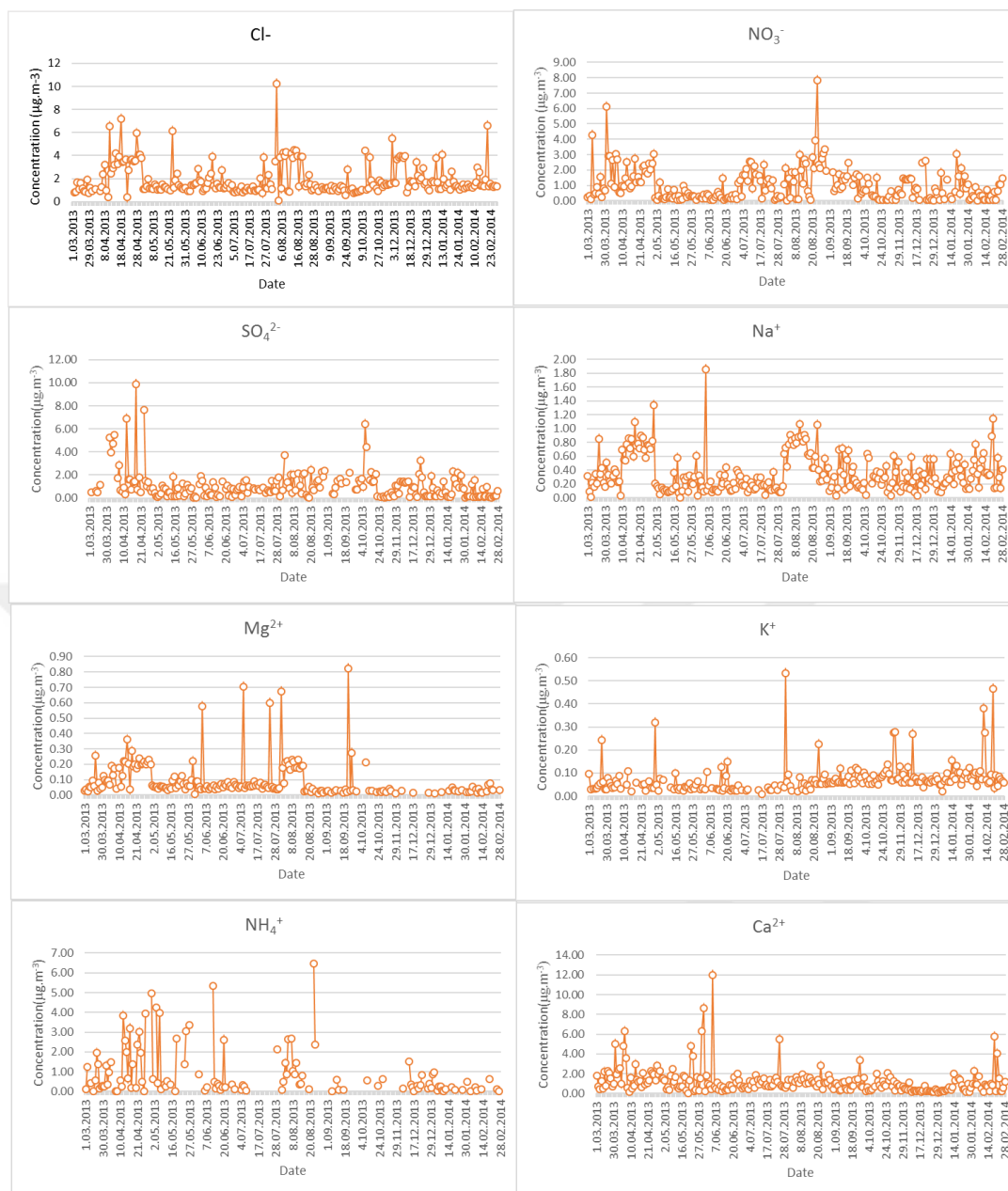


Figure 4.9. Temporal variations of ions in PM_{2.5-10}

The city is cold in winter and cool in summer especially at high altitude areas. In addition, people live in high altitude areas (Bolu Environmental Status Report, 2010) use the biomass for heating processes. Therefore, K⁺ concentrations increased after August in PM_{2.5} and in PM_{2.5-10}.

In PM_{2.5}, sulfate, Cl⁻, Na⁺, Ca²⁺ and Mg²⁺ concentrations were higher in April and in August 2013. Sulfate concentrations were also higher in July 2013. In PM_{2.5-10},

chloride ion, Na^+ and Mg^{2+} concentrations increased in April and in August 2013. The concentrations of Ca^{2+} increased in some spring season days in coarse particles.

$\text{NO}_3^-/\text{SO}_4^{2-}$ and $\text{SO}_4^{2-}/\text{K}^+$ give information about anthropogenic sources. Figure 4.10 and 4.11 show the temporal variations of $\text{NO}_3^-/\text{SO}_4^{2-}$ and $\text{SO}_4^{2-}/\text{K}^+$ in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$. If the $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio is greater than one, emissions from mobile sources has greater contributions. On the other hand, if the ratio is lower than one, sampling area is affected by sources from industrial activities or coal burning (Arrimato et al., 1996; Wang et al., 2006). $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio arithmetic mean in $\text{PM}_{2.5}$ and in $\text{PM}_{2.5-10}$ are 0.11 ± 0.13 and 0.38 ± 0.34 , respectively. These values show that coal burning was effective in the sampling site. The ratios in each day were lower than one in $\text{PM}_{2.5}$ except one day. However, the ratios of some $\text{PM}_{2.5-10}$ samples were greater than one. Traffic emissions can cause high NO_3^- concentrations.

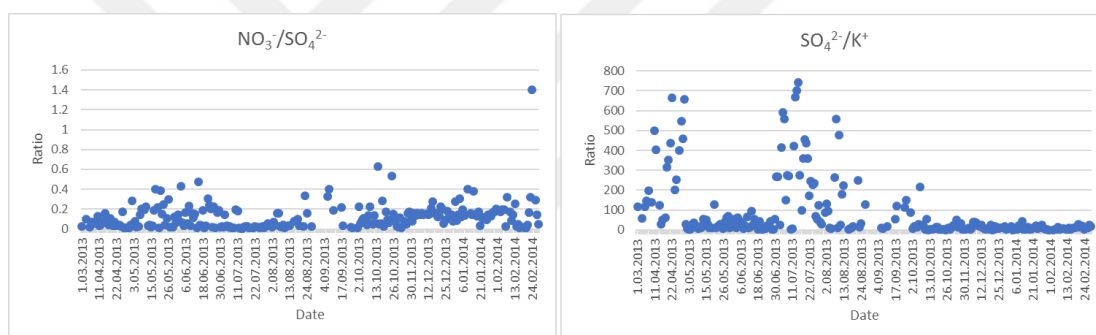


Figure 4.10. $\text{NO}_3^-/\text{SO}_4^{2-}$ and $\text{SO}_4^{2-}/\text{K}^+$ ratios in $\text{PM}_{2.5}$

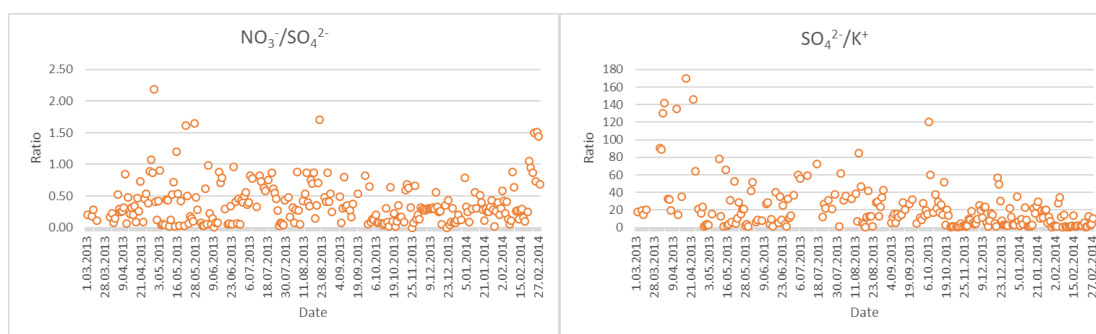


Figure 4.11. $\text{NO}_3^-/\text{SO}_4^{2-}$ and $\text{SO}_4^{2-}/\text{K}^+$ ratios in $\text{PM}_{2.5-10}$

The $\text{SO}_4^{2-}/\text{K}^+$ ratios give the information about burning activities. Low $\text{SO}_4^{2-}/\text{K}^+$ ratio indicates the biomass and straw burning (Watson et al., 2001; Shen et al., 2009). The ratio were higher in April and summer season because of the higher SO_4^{2-} concentrations in those days in $\text{PM}_{2.5}$. Back trajectories of days having high sulfate concentrations were evaluated and the effects of air mass flow coming from Black Sea was observed. There are dimethyl sulfide (DMS)-producing species in Black Sea (Kubilay et al., 2002) and those species, concentrations change seasonally. Low algal and high dimethylsulfoniopropionate (DMSP) conditions affect the DMS cycling rates and this affect is called as summer maxima paradox. DMS in water goes into air and DMS in air was converted to sulfate and sulfonate aerosols with solar radiations and high temperature. Then it is transported to the other part of the regions. In addition, there was a movement of Saharan dust before the increase in SO_4^{2-} concentration because desert Fe(II) causes pytoplankton bloom, especially *Emiliania huxleyi* and growing cycle is completed in 6 or 7 days (Saydam and Polat, 1999). Therefore SO_4^{2-} concentrations were higher in the seasons having higher temperature in $\text{PM}_{2.5}$ and in $\text{PM}_{2.5-10}$ in April and in July.

4.5.1 Correlations between anions and cations in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$

Neutralization of atmospheric particles were evaluated by using the ratio of major cations to anions in equivalent ($R_{C/A}$) (He et al., 2012). If the ratio is higher than one, the particles are alkaline. On the other hand, the particles are acidic if the ratio is lower than one. In that study, $R_{C/A}$ is calculated firstly using the total concentration in $\mu\text{eq.m}^{-3}$. The anion and cation microequivalents were calculated as;

$$\text{Anion}(\mu\text{eq.m}^{-3}) = \frac{\text{Cl}^-}{35.5} + \frac{2(\text{SO}_4^{2-})}{96} + \frac{\text{NO}_3^-}{62}$$

$$\text{Cation}(\mu\text{eq.m}^{-3}) = \frac{\text{Na}^+}{23} + \frac{\text{NH}_4^+}{18} + \frac{\text{K}^+}{39} + \frac{2x(\text{Mg}^{2+})}{24} + \frac{2x(\text{Ca}^{2+})}{40}$$

The correlations of between anion and cation were calculated. However, the correlations between anions and cations were low in $\text{PM}_{2.5-10}$ and $\text{PM}_{2.5}$ (Figure 4.12). Because of the findings about possibility of Black Sea effect in Figure 4.10 and 4.11,

the non-sea salt concentrations of anions and cations were also calculated by using the equation

$$C_{nssi} = C_{total} - \left(\frac{C_{swi}}{Na_{sw}^+} \right) Na_s^+$$

where C_{nssi} is the nss concentration of i th anion or cation in $\mu\text{g.m}^{-3}$, C_{total} is the total concentration of i th anion and cation in $\mu\text{g.m}^{-3}$, C_{swi} is the concentration of i th anion or cation in sea water, Na_{sw}^+ is the Na^+ concentration in sea water and Na_s^+ is the concentration of Na^+ in PM samples. The ratio of $\left(\frac{C_{swi}}{Na_{sw}^+} \right)$ is equal 1.81 for Cl^- , 0.038 for Ca^{2+} , 0.129 for Mg^{2+} , 0.036 for K^+ and 0.253 for SO_4^{2-} (McInnes et al.,1996). There was not a significant increase in correlation between the anion and cation by using non-sea salt components. Therefore, $R_{C/A}$ was calculated as;

$$R_{C/A} = \frac{[NH_4^+]_{eq} + [K^+]_{eq} + [Ca^{2+}]_{eq} + [Mg^{2+}]_{eq}}{[Cl^-]_{eq} + [SO_4^{2-}]_{eq} + [NO_3^-]_{eq}}$$

The calculated average $R_{C/A}$ in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ were 1.14 ± 0.63 and 1.13 ± 0.58 , respectively.

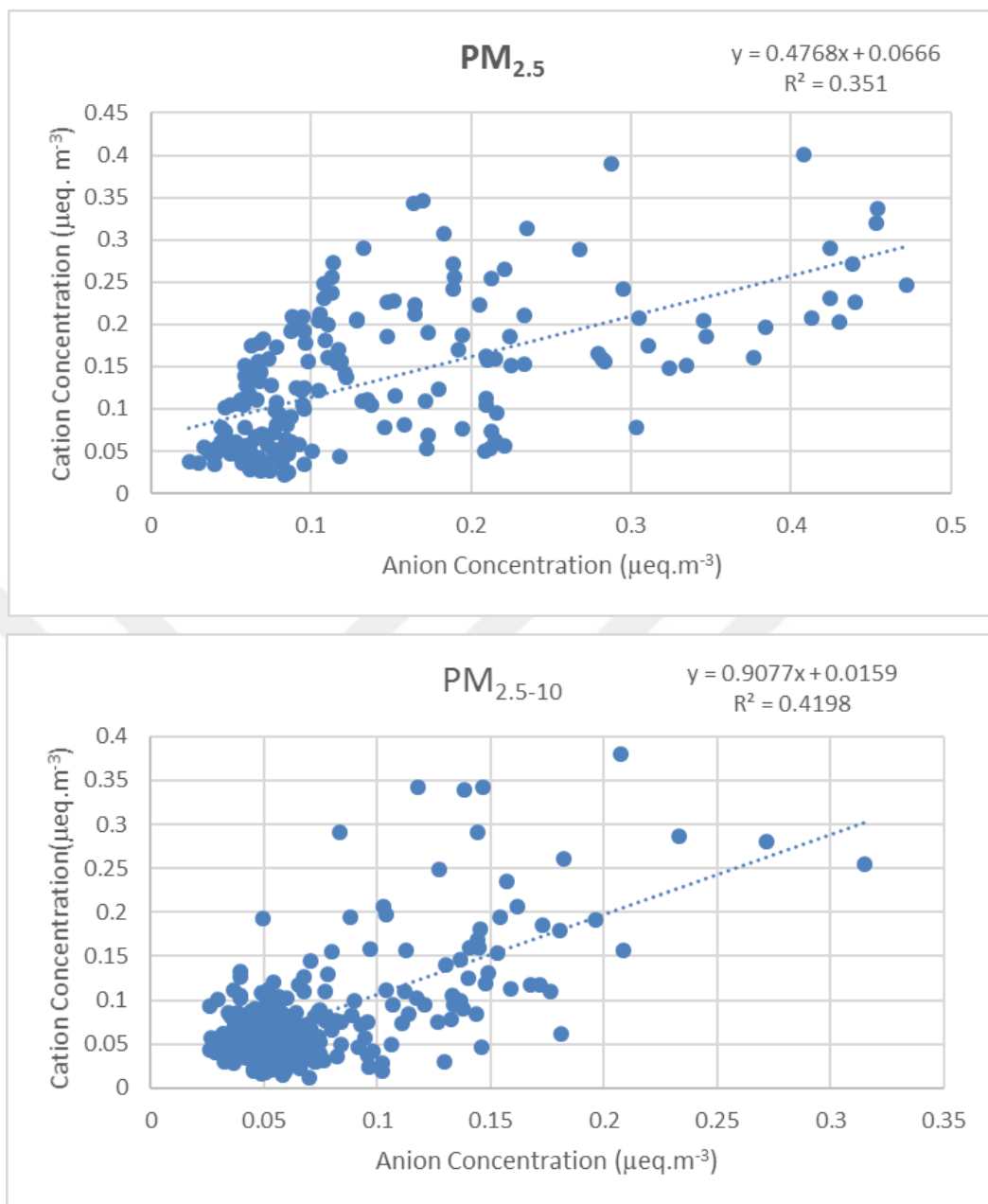


Figure 4.12. Correlations between anions and cations

Temporal variations of total anion and cation concentrations in $\mu\text{eq. m}^{-3}$ and the $R_{C/A}$ values are shown in Figure 4.14 and in Figure 4.15. It was observed that the $R_{C/A}$ values decreased when the anion and cation concentrations increased. Total ion concentrations were higher in April and in July in $PM_{2.5}$ whereas they were higher only in July in $PM_{2.5-10}$. Lower $R_{C/A}$ values were observed in April, July and December in $PM_{2.5}$ and in June and in October in $PM_{2.5-10}$. As a result, the acidic particles were observed in the sampling site.

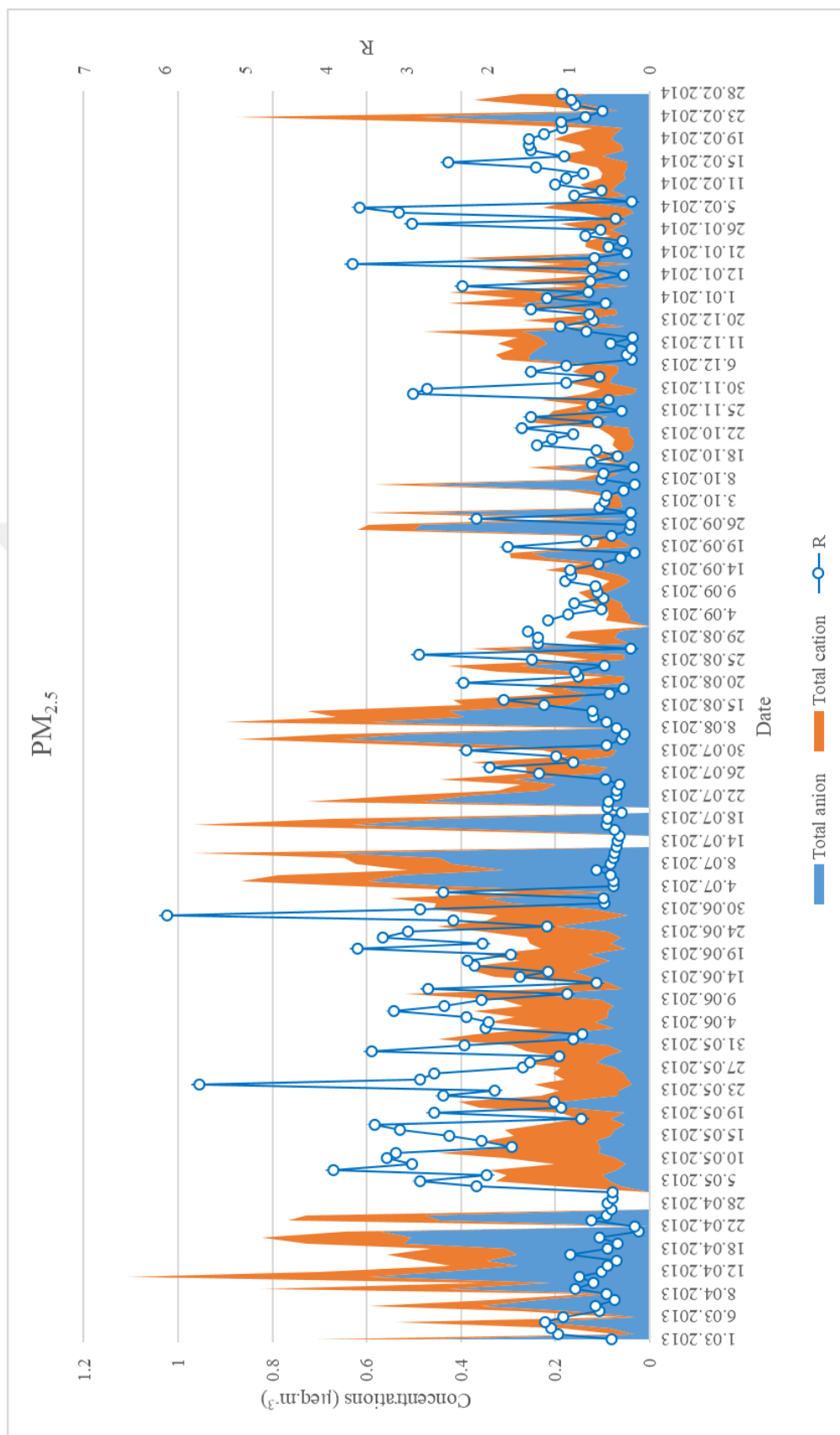


Figure 4.13. Temporal variations of the $R_{C/A}$ values in $PM_{2.5}$

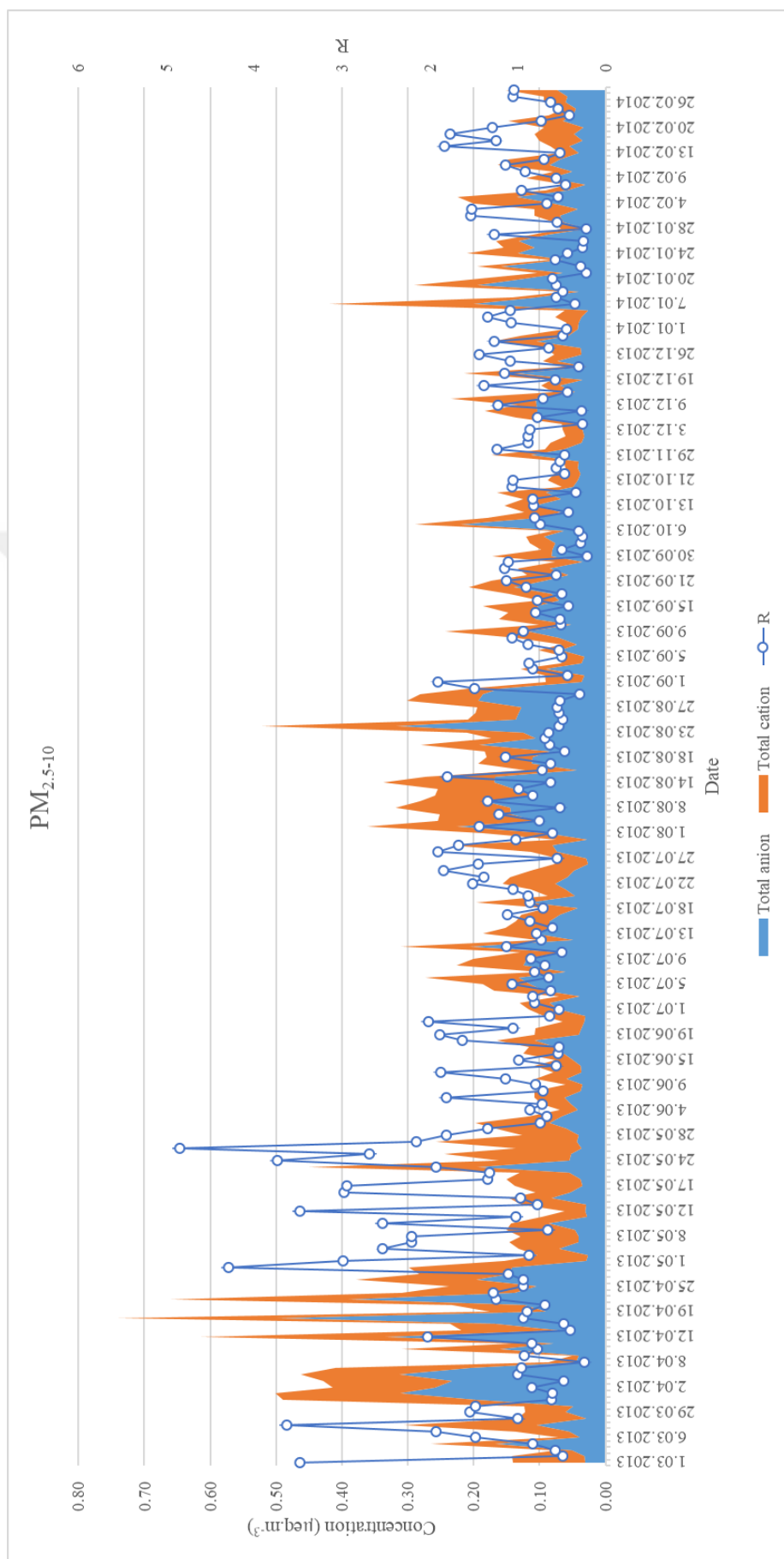


Figure 4.14. Temporal variations of the $R_{C/A}$ values in $PM_{2.5-10}$

4.5.2 Multiple linear regression

A multiple linear regression analysis was performed to evaluate acid base chemistry in PM_{2.5} and PM_{2.5-10} samples. Sulfate and NO₃⁻ were dependent variables and Ca²⁺, Mg²⁺ and NH₄⁺ were independent variables. Table 4.5 and 4.6. showed the multiple linear regression parameters for SO₄²⁻ and NO₃⁻ against Ca²⁺, Mg²⁺ and NH₄⁺. The explained percent values for SO₄²⁻ and NO₃⁻ in PM_{2.5-10} were 18.7 and 37.2 by Ca²⁺, Mg²⁺ and NH₄⁺. On the other hand, 14.7% SO₄²⁻ and 0.293% of NO₃⁻ can be explained by the cations in PM_{2.5} samples. In addition, there were no significant effect of Ca²⁺ in neutralization in PM_{2.5}.

Table 4.5. Multiple linear regression parameters for SO₄²⁻ and NO₃⁻ in PM_{2.5-10} samples

Sulfate	[SO ₄ ²⁻] = a+α ₁ [Ca ²⁺] +α ₂ [Mg ²⁺] +α ₃ [NH ₄ ⁺]		
A	0.00713	r ²	0.187
α ₁	0.213	% of r ² explained by Ca ²⁺	87.9
α ₂	0.784	% of r ² explained by Mg ²⁺	5.93
α ₃	0.00713	% of r ² explained by NH ₄ ⁺	6.12
Nitrate	[NO ₃ ⁻] = a+β ₁ [Ca ²⁺] + β ₂ [Mg ²⁺] + β ₃ [NH ₄ ⁺]		
B	0.00057	r ²	0.372
β ₁	0.054	% of r ² explained by Ca ²⁺	76.3
β ₂	0.0956	% of r ² explained by Mg ²⁺	18.6
β ₃	0.00722	% of r ² explained by NH ₄ ⁺	13

Table 4.6. Multiple linear regression parameters for SO₄²⁻ and NO₃⁻ in PM_{2.5} samples

Sulfate	[SO ₄ ²⁻] = a+α ₁ [Ca ²⁺] +α ₂ [Mg ²⁺] +α ₃ [NH ₄ ⁺]		
A	0.00409	r ²	0.147
α ₁	-0.383	% of r ² explained by Ca ²⁺	0
α ₂	5.74	% of r ² explained by Mg ²⁺	38.5
α ₃	0.568	% of r ² explained by NH ₄ ⁺	61.4
Nitrate	[NO ₃ ⁻] = a+β ₁ [Ca ²⁺] +β ₂ [Mg ²⁺] +β ₃ [NH ₄ ⁺]		
B	0.00267	r ²	0.00293
β ₁	0.000279	% of r ² explained by Ca ²⁺	32.9
β ₂	0.158	% of r ² explained by Mg ²⁺	54.1
β ₃	0.000818	% of r ² explained by NH ₄ ⁺	13.1

4.6 Concentrations of carbonaceous species

OC and EC analyses were performed in PM_{2.5} and PM₁₀ samples in quartz filters collected for six months (September 2013-February 2014). A total of 166 of PM_{2.5} and 172 PM₁₀ samples were collected. The highest EC and OC values were observed in December 2013, as the lowest temperature was observed in that month, the heating process had increased. For this reason, the amount of elemental and organic carbon was higher in this month. The arithmetic means of OC and EC concentrations in PM₁₀ samples are larger than that of PM_{2.5} samples.

The temporal variations of OC and EC were illustrated in Figure 4.15 and 4.16. The concentrations of EC and OC increased in December both in PM₁₀ and PM_{2.5} due to increase in heating processes in that month. No significant difference was observed between the concentrations of both EC and OC in different particulate size ranges. Two types of particles showed almost the same trend.

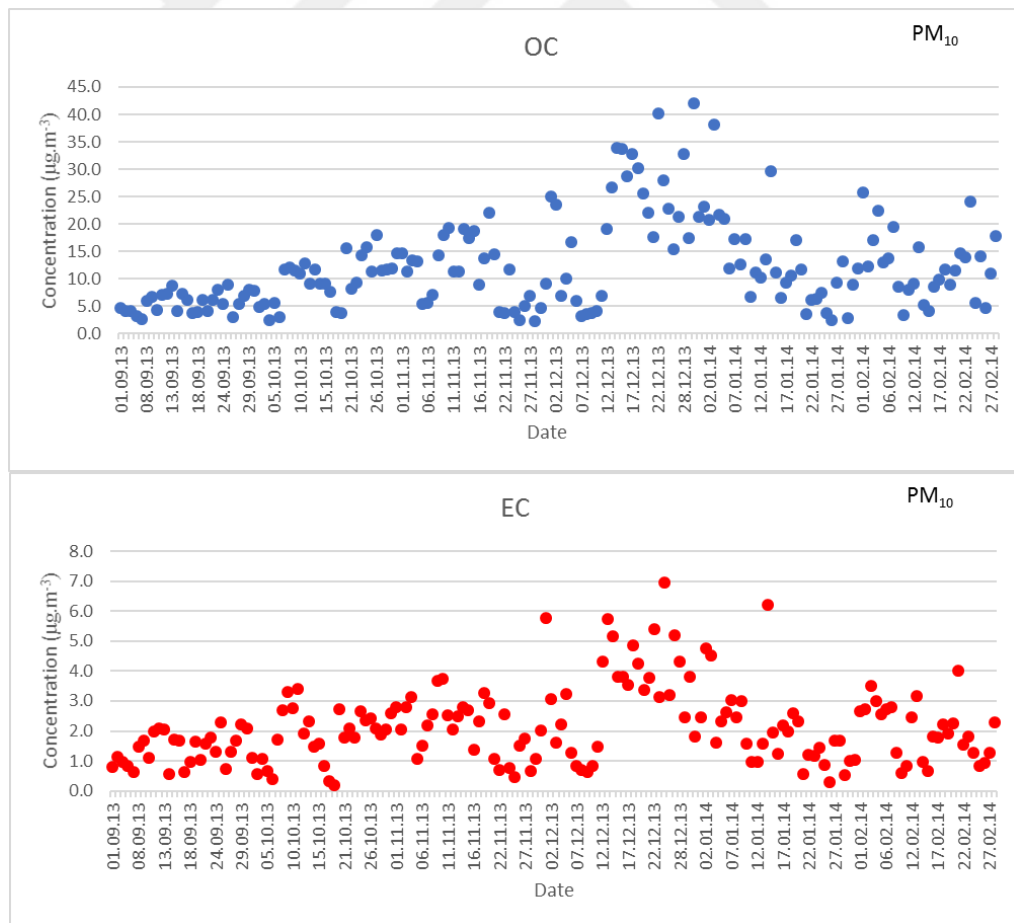


Figure 4.15. Temporal variations of EC and OC concentrations in PM₁₀ samples

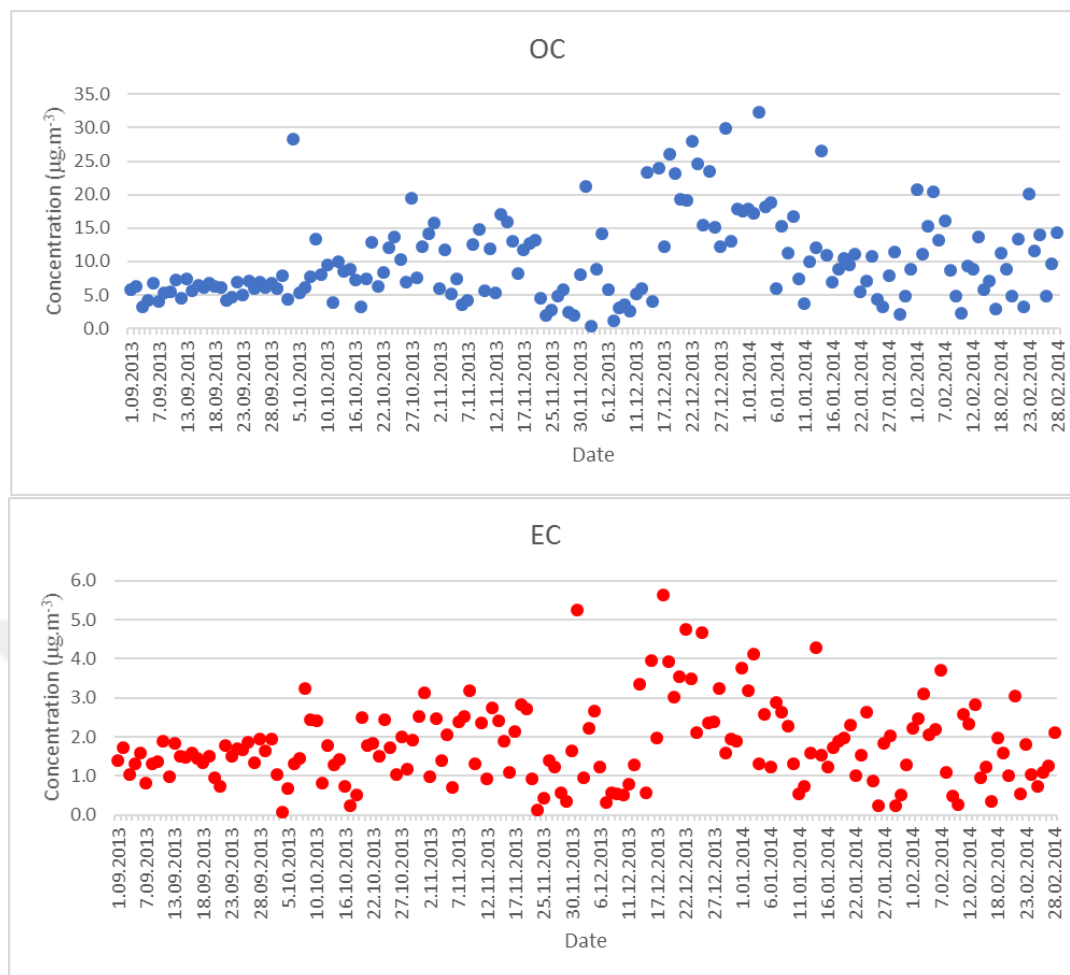


Figure 4.16. Temporal variations of EC and OC concentrations in PM_{2.5} samples

4.6.1 Correlations between EC and OC

The correlation between EC and OC is related with the emissions from a dominant primary source (Na et al., 2004). The correlation between EC and OC values in our study were illustrated in Figure 4.17. The correlation coefficients in PM_{2.5} and PM₁₀ samples for whole samples were 0.68 and 0.71, respectively. The correlation between EC and OC values for each month was shown in Figure 4.18. The highest coefficients were observed in September for PM_{2.5} and PM₁₀ samples. The lowest correlation was observed in December and February in PM₁₀ samples. However, there was significant decrease in correlation in October and in February in PM_{2.5} samples (Figure 4.19). Coal combustion was a dominant source in Bolu and this dominant source might have been effective in September for PM₁₀.

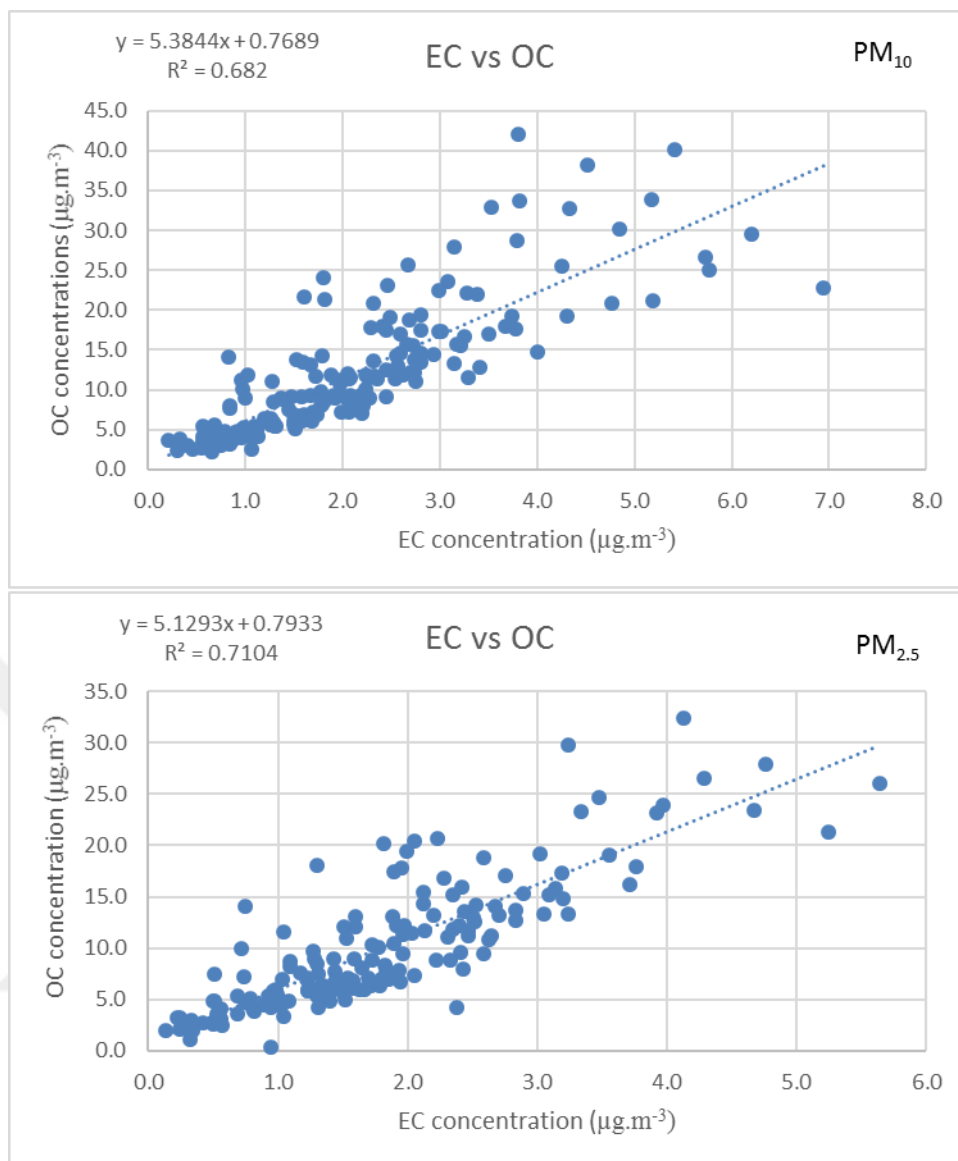


Figure 4.17. Correlations between OC and EC values

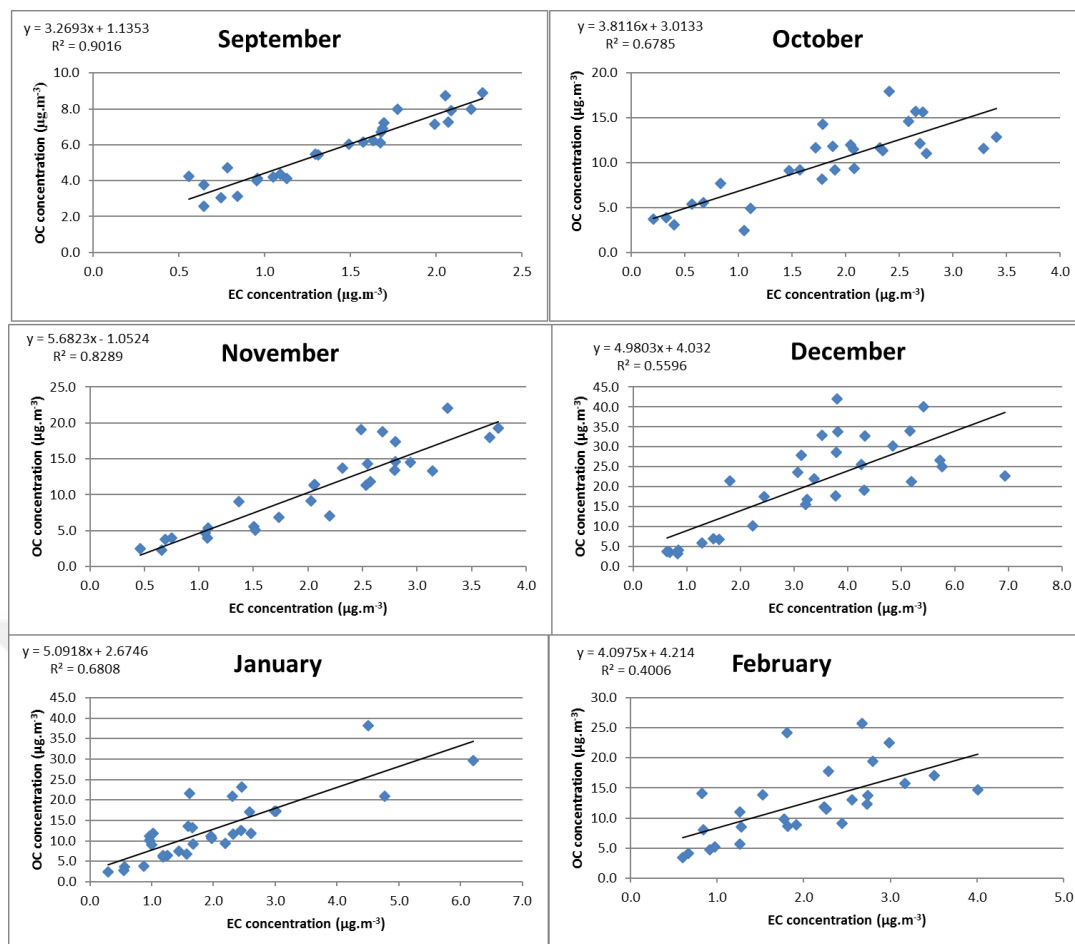


Figure 4.18. Correlations between EC and OC values in PM₁₀ samples in each month

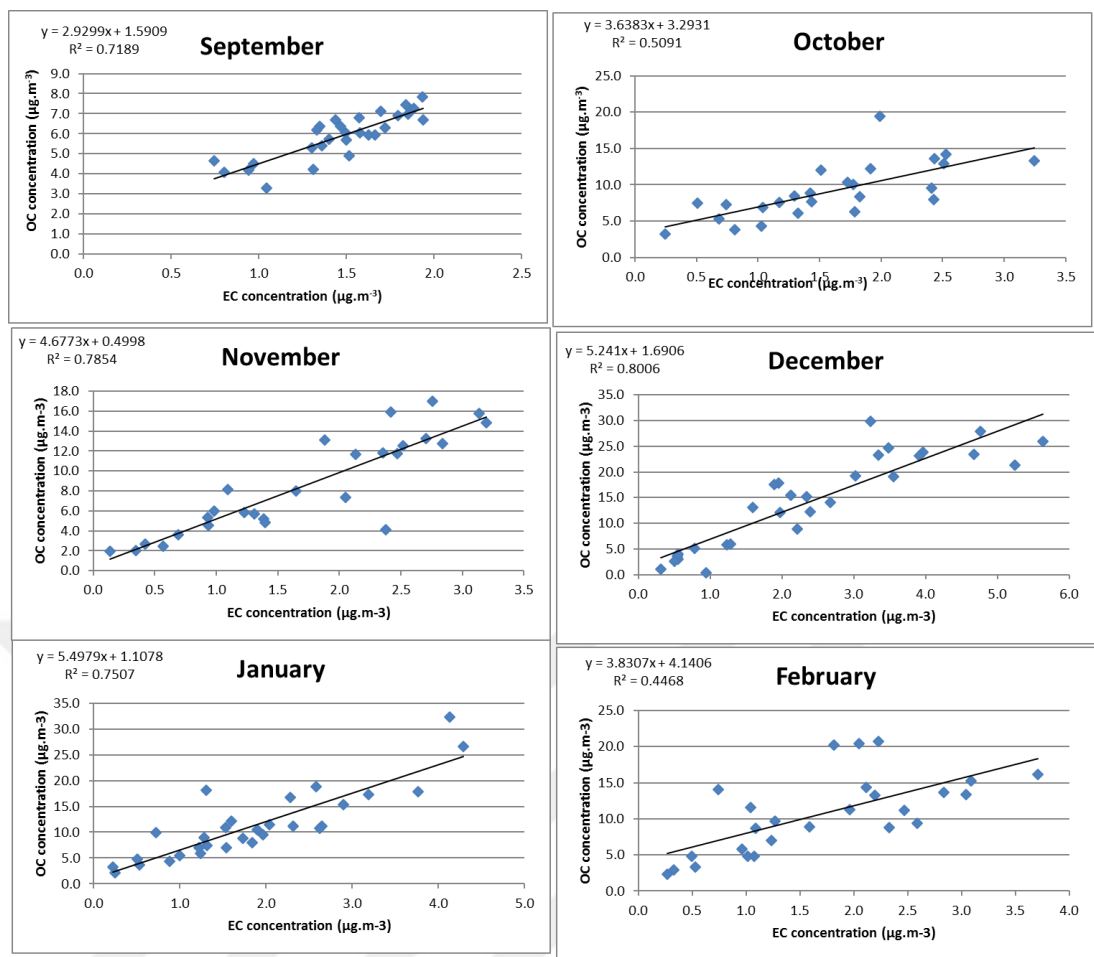


Figure 4.19. Correlations between EC and OC values in $\text{PM}_{2.5}$ samples in each month

4.6.2 Determination of OC_{pri} and OC_{sec} in $\text{PM}_{2.5}$

Secondary aerosol particles in the atmosphere are an organic matter produced from oxidation of organic compounds. It is an important task to determine their relationship with fine PM.

OC_{sec} and OC_{pri} were calculated by using EC-OC tracer method. The important step of the method is to determine the $(\text{OC}/\text{EC})_{\text{pri}}$ ratio for the sampling site. The method of taking the minimum OC/EC ratio during the sampling period was suitable for calculation in sampling area. The minimum OC/EC ratio was 1.74. Temporal variations of OC_{pri} and OC_{sec} were illustrated in Figure 4.20. The concentrations of OC_{pri} and OC_{sec} increased with an increase in heating season. Fossil fuel emissions, biomass burning or biological particles or plant debris are the sources of OC_{pri} .

However, low photochemical activity should have taken into account for large urban areas on some days especially during winter days (Pio et al., 2011). The primary process was initiated by reaction between the species such as the OH, NO₃ and O₃ radical. Then oxidation of a VOC can produce species of sufficiently low vapor pressure to be condensable, leading to the formation of OC_{sec} and products of higher volatility CO₂ and CH₂O (Kroll and Seinfeld, 2008). Another parameter, mixing layer height, is an important parameter for the determination of air pollution in urban atmosphere which has a strong source besides meteorological parameters. It defines the volume for the dilution of air pollutants emitted (Schäfer et al., 2006). Bolu had the lower mixing height values (400 m) in winter than that in summer (700 m) (Özlü, 2014). Therefore, the produced organics can not be dispersed and accelerates the formation of the secondary organic compounds (Strader, 2000). Because of the chemical complexity of these oxidation processes, the exact chemical mechanisms of the formation mechanism did not well understand (Kroll and Seinfeld, 2008). The concentrations of OC_{pri} were generally lower than OC_{sec} concentrations. OC_{pri} concentrations were higher than OC_{sec} concentrations in samples collected on the days of 04/09/2013, 05/09/2013, 23/09/2013, 28/09/2013, 9/10/2013, 7/11/2013, 26/11/2013, 2/12/2013, 7/12/2013.

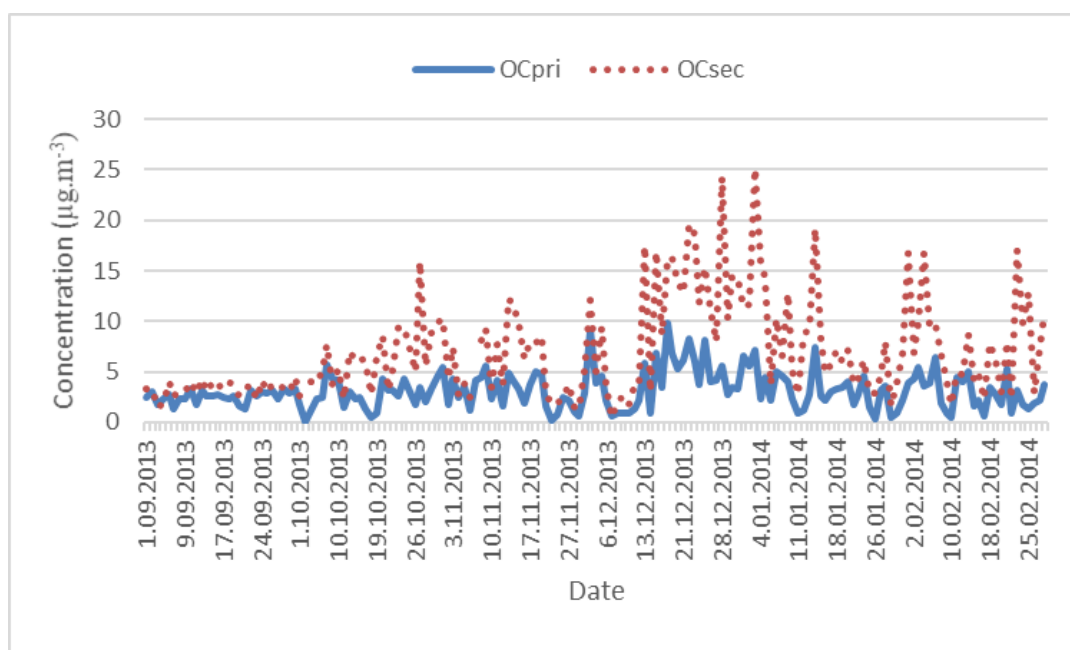


Figure 4.20. Temporal variations of OC_{pri} and OC_{sec} values in PM_{2.5} samples

4.7 Seasonal variations of PM

Meteorological parameter like temperature, wind speed, wind direction, solar radiation, total rain and relative humidity were measured during the sampling period. Monthly statistics were shown in Table 4.7. Temperature of the sampling area in the sampling period were between (-7.8°C) and 23.1°C. The minimum temperature was observed in December 2013 and the maximum temperature was observed in May 2013. The monthly average temperature were between (-1.1)°C and 18.8°C. The lowest monthly average temperature was observed in December 2013 and the highest monthly average temperature was observed in August 2013. Wind speed varied from 0.4 m/s to 3.2 m/s during the study period. The lowest and highest monthly average wind speed was recorded in December 2013 and in July 2013, respectively. The humidity ranged between 33.7 to 99% during the study period. The monthly cumulative rainfall ranges between 18.1-1.1 in the sampling period. Maximum rainfall was observed in March 2013 and minimum was recorded in November 2013. The solar radiation in the sampling period were between 572 W.m⁻² and 25 W. m⁻². The coldest month also had the lowest solar radiation. Therefore, there was not any significant difference between months in the sampling season and heating process was a continuous process in Bolu in the sampling season. Peoples used heating processes mostly in the evenings in warmer months like June, July, August and September. June-2013- September 2013 was selected for nonheating season and March 2013- May 2013 and October 2013- February 2014 periods were selected for heating season.

Figure 4.21 was illustrated the nonheating season to heating season ratios of arithmetic mean of elements and ions in PM_{2.5} and PM_{2.5-10} aerosols. Hafnium, NO₃⁻, W, NH₄⁺, Mn, Na, Na⁺ were greater than unity in two types of particles. Iron, Ce, Mg²⁺, La, Cd, Hg, Cs, Rb, Pr, Th, Yb, Mg, Er, Y in PM_{2.5-10} and Lu, SO₄²⁻, Tm, Ni, Cr, Zn in PM_{2.5} were greater than unity. There was not a significant arithmetic mean difference in Sc, Cs, Yb, Al, Be, Pb, Mg, Ca, Cl⁻, Er, Fe for PM_{2.5} and Li, Ca²⁺, Co, Ti, K, Dy, Ca, U, Ni, Mo, Nd, Cr, SO₄²⁻, Sm, Cd, Al, Cl⁻, Sn, Zn, Sc for PM_{2.5-10}. Se, V, As concentrations were higher in heating season than in non-heating season.

Table 4.7. Meterological parameters in the sampling period

		T	WS	Total rain	SR	RH
		(°C)	(m/s)	mm	(W/m²)	(%)
March 2013	avg ± std	6.6± 5.4	1.8 ± 0.7	18.1	260 ± 95.0	73.3 ± 17.8
	Range	17.4-(-4.0)	3.2-0.7	3.8-0.3	426-86.2	98.6-33.7
April 2013	avg ± std	9.8 ± 4.8	2.0 ± 0.6	9.48	327 ± 165	76.9 ± 16.0
	Range	17.5-2.9	3.1-0.9	3.00-0.9	529-63.1	97.7-45.5
May 2013	avg ± std	15.7 ± 2.6	2.1 ± 0.6	13.1	234± 97.2	75.3 ± 12.3
	Range	23.1-10.5	3.8-0.7	2.6-0.3	527-234	96.1-45.3
June 2013	avg ± std	16.6 ± 2.7	2.2 ± 0.5	10.9	422± 103	79.7± 8.0
	Range	22-11.8	3.3-1.3	3.8-0.3	572-181	94.7-60.2
July 2013	avg ± std	18.3 ± 1.7	2.4 ± 0.4	1.66	406 ± 102	81.2± 8.2
	Range	21-14.4	3.5-1.5	0.5-0.3	498.7-85.7	93.6-61.6
August 2013	avg ± std	18.8 ± 1.5	2.3 ± 0.5	3.48	452± 94.7	78.4 ± 7.4
	Range	21.3-13.2	3.3-0.5	0.8-0.3	543-115	97-60.5
Septemb er 2013	avg ± std	13.9 ± 2.7	2.0± 0.4	5.67	335± 93.7	78.7± 9.4
	Range	21.1-9.5	3.2-1.3	2.4-0.3	457-168	96.4-60.5
October 2013	avg ± std	8.7 ± 3.9	1.9± 0.6	12.5	291±105	79.3 ± 13.4
	Range	16.9-0.8	3.2-1	4.6-0.3	417-91.5	97.8-56.3
Novembe r 2013	avg ± std	7.8 ± 3.7	1.3 ± 0.5	1.1	233 ± 74.5	74.4± 13.2
	Range	13.9-0.8	2.6-0.6	0.7-0.4	325-72	94.6-51.3
Decembe r 2013	avg ± std	-1.1 ± 3.9	1.1± 0.8	3.7	167.6± 75.4	79.9 ± 13.3
	Range	5.6-(-7.8)	2.9-0.4	0.8-0.3	267-25	98.4-51.2
January 2014	avg ± std	4.0 ± 3.0	1.2 ± 0.5	7.97	161.4 ± 55.5	80.9 ± 11.3
	Range	10-(-2.8)	2.6-0.4	1.3-0.3	262-55.5	98.3-53.5
February 2014	avg ± std	4.4 ± 4.1	1.8 ± 0.7	7.1	246± 87.2	76.1± 14.8
	Range	10.1- (-2.4)	3.6-0.8	1.5-0.3	342.2-47.6	99-51.4

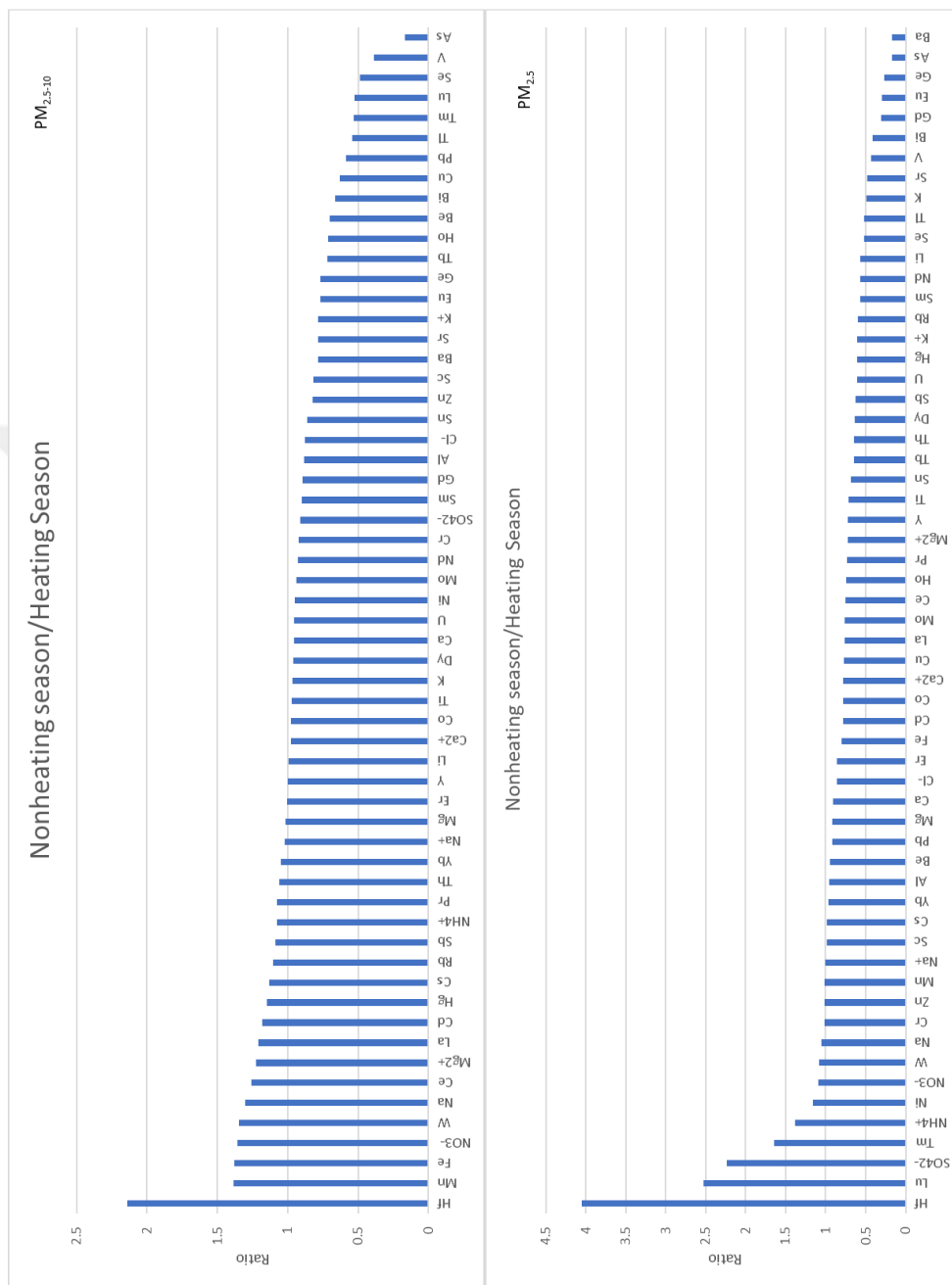


Figure 4.21. Nonheating/heating season ratios of arithmetic mean in PM_{2.5} and PM_{2.5-10}

4.8 Comparison of results with literature values

In that study, different types of sampling site in different countries were used for comparison to investigate the pollution levels in our sampling area. Arithmetic means of each parameter were used for evaluations. In addition, elements, ions and carbonaceous species were evaluated separately in $PM_{2.5-10}$ and $PM_{2.5}$.

Concentrations of $PM_{2.5-10}$ were compared with Denver (USA) (Clements et al., 2014), Eskişehir (Gaga et al., 2012), Central Los Angeles, California (Cheung et al., 2011). In addition, the studies in Erdemli (Koçak et al., 2007), İzmir (Kara et al., 2015), Bolu (Sağırılı, 2013; Özlü, 2015) were also used. In addition, the concentrations of $PM_{2.5}$ were compared with Denver (USA) (Clements et al., 2014), Košetice, Czech Republic (Schwarz et al., 2016), Erdemli (Koçak et al., 2007), Eskişehir (Arı et al., 2015), Bolu (Sağırılı, 2013; Özlü, 2015). The properties of studies are described below.

a) Denver (USA) (Clements et al., 2014)

Daily $PM_{10-2.5}$ and $PM_{2.5}$ were collected for six-day periods between February 2010 and March 2011 in Denver and in Greeley, Colorado. Denver was affected from industrial and motor vehicle emissions. On the other hand, Greeley had highly agricultural activity. Dichotomous samplers with teflon filters were used for sampling. The samples were analysed by using ICP-MS. Totally 49 elements were determined.

b) Eskişehir, (Arı et al., 2015)

$PM_{2.5}$ aerosol samples were collected between 1 October 2013 and 10 June 2014 in the campus of Anadolu University in Eskişehir. High volume sampler with $PM_{2.5}$ impactor was used for sampling. 45 elements and organic components of the PM were determined and results were statistically evaluated (Arı et al., 2015).

c) Central Los Angeles, California (Cheung et al., 2011)

In the study, sampling was made in ten different sampling sites in Los Angeles. PM_{10} samples were collected on quartz filters by using cascade impactor. The samples

were analyzed by using ICP-MS. Element concentrations of samples collected in Central Los Angeles were compared in our studies.

d) Košetice, Czech Republic (Schwarz et al., 2016)

Košetice is a rural background site in Czech Republic. Elemental composition (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, and Pb) and the concentration of water-soluble inorganic anions (SO_4^{2-} , NO_3^- , Cl^- , NO_2^- , Br^- , and H_2PO_4^-) and cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+}), elemental and organic carbon (EC and OC), and levoglucosan were determined. Average concentrations of individual species were similar with other parts of the Europe. $\text{PM}_{2.5}$ contained largely water soluble inorganic ions and organic matter. Seasonal differences were found because of the heating process (wood and coal combustion). Air masses were also investigated by wind sector analysis and back trajectories (Schwarz et al., 2016).

e) İzmir, Turkey (Kara et al., 2007)

Source apportionment studies were done by using concentration of elements at Industrial site, Izmir, Turkey. The PM_{10} samples were collected on PTFE filters by using dichotomus sampler for 24 hours. The samples were analyzed in ICP-MS. A total of 456 PM_{10} samples were analyzed. The winter and summer trace concentrations in industrial sites were used for comparison.

f) Erdemli, Turkey (Koçak, 2007)

Stacked filter unit was used to collect daily $\text{PM}_{2.5}$ and PM_{10} samples at a rural site, Erdemli, between April 2001 and April 2002. Totally 562 filter samples were collected. Water soluble ions and elements were analyzed by using ion chromatography and PIXE, respectively.

g) Eskişehir, Turkey (Gaga et al., 2012)

PM_{10} samples were collected by high volume PM_{10} sampler. Two samplers were used simultaneously in urban (E-1) and urban-traffic (E-2) stations. Mass concentrations of $\text{PM}_{2.5}$ and PM_{10} , PAH concentrations, NO_x and SO_2 concentrations by passive samplers were also determined in the study.

h) Bolu, Turkey (Özlü, 2015)

The daily aerosol samples were collected between March 2009 and March 2010 by using the same sampling instrument at the same sampling station. The collected samples were analyzed for elements, ions, OC, and EC.

i) Bolu, Turkey (Sağırlı, 2013)

The daily aerosol samples were collected between February 2011 and February 2012 from the same sampling station of this study. The stack filter units were used for sampling. The collected samples were analyzed for elements by using ICP-MS.

The results of explained studies were summarized in Table 4.8 and Table 4.9.

PM_{2.5} mass concentration was 2 times higher than rural site in Erdemli and suburban site in Denver. However, the mean concentration of PM_{2.5} in Beijing was higher than our study. Furthermore, PM_{2.5-10} concentrations in Denver were also lower than our study. Highly industrialized city Beijing had higher PM₁₀ concentrations than this study.

Arithmetic mean of the PM concentrations in our study was nearly two times higher than mean values found in Denver. Mean concentrations of Na, Al, K, Ca, Fe, Cu, Zn, As, Pb in Denver for PM_{2.5} and PM_{2.5-10} were lower than our study. Arithmetic mean values of La and Sb for two types of particles were close to values found in our study.

Košetice is the rural area in Czech Republic. There is a major national highway near the city. In addition, there is a small wood factory in the area. PM_{2.5} concentration was similar with our study. However, element, ion and OC and EC concentration was lower than our study except Zn, NO₃⁻, and Pb concentration.

Eskişehir is an urban area in Central Anatolian Region of Turkey. Coal was still used in the sampling period for heating and industrial purposes. However, concentrations of coal burning tracer element, As, were lower than studies done by Ari et al., 2015. Arithmetic mean concentrations of Mg, Co, Zn, Sr, Cd, Sb, La, Pb were similar with our study.

Table 4.8. Literature comparison of PM_{2.5} (ng.m⁻³)

	Denver, USA ^a	Eskişehir ^b	Košetice ^d	Erdemli ^f	Bolu ^h	Bolu ⁱ	This study
Property of area	Suburban	Urban	Rural	Rural	Semi- urban	Semi- urban	Semi- urban
PM _{2.5} *	6.84	48	15.7	9.7	17.5	17.7	16.8
Na	29	1150			217	581	412
Mg		320			972	73	298
Al	42	299.40	30.2		1670	1342	1020
K	41	59.6	108	116	354	184	172
Ca	48	129	12.3	158	2830	756	715
Ti		70	2.1	4.1	128	11	12.7
V		2.49		4.5	4	1	1.4
Cr		2.54		1.8	20	20	34.3
Mn		80	1.46	7.6	11	4	4.76
Fe	89	111	28.8	53.3	295	199	300
Co		0.26			2	2	0.27
Ni				1.6	35	6	7.1
Cu	2.4		0.89		10	6	3.09
Zn	13	12.7	15.2	4.9	38	27	16.7
As	0.2	0.56	0.7		2	1	2.4
Se		0.15			0.2	0.4	0.47
Sr		1.38				4	1.43
Y					0.1	0.05	0.04
Mo					3	0.3	0.41
Cd		0.14			1	5	0.16
Sb	0.47	0.68			1.4	1	0.4
La	0.24	0.22			0.2	0.2	0.2
Pb	1.1	4.89	4.9		20	12	5.2
Bi		0.02			0.3	0.1	0.08
Cl ^{-*}			0.04	0.108	2.1		2.34
NO ₃ ^{-*}		2.43	2.2	0.268	0.81		0.278
SO ₄ ^{2-*}		2.80	2.85	6.75	3.6		6.24
NH ₄ ⁺ *				0.850	1.6		2.33
Na ⁺ *			0.037	0.339	0.59		0.491
K ⁺ *			0.092	0.108	0.1		0.123
Mg ^{2+*}			0.004	0.054	0.046		0.117
OC*			4.1		7		10.1
EC*			0.6		1.6		1.79

^a Clements et al., 2014 ^b Arı et al., 2015 ^d Schwarz et al., 2016 ^f Koçak, 2007 ^h Özlü, 2015 ⁱ Sağrılı, 2013

*

means µg.m⁻³

Table 4.9. Literature comparison of PM_{2.5-10}

	Denver, USA ^a	Eskişehir ^b _x	Central Los Angeles _c				
	Suburban	Urban- Traffic Winter	Urban	İzmir ^{e, x} Industrial	Bolu ^g Semi- urban	Bolu ^h Semi- urban	This study Semi- urban
PM _{2.5-10} [*]	7.90	120.7	10.1	39.9	13	15.4	11.6
Na	88			918		310	307
Mg		827	118	508		128	276
Al	96	1045	192	1198		1393	990
K	80			604	290	290	100
Ca	100		243	2241		1494	1088
Ti			23.5			22	23.8
V		3.6		15.6	3.2	1	1.51
Cr		7.3		33.3	23	11	27.4
Mn		21.0		75.5	10	5	6.33
Fe	130	972	397	1832	310	237	382
Co		0.7		0.73	2.1	2	0.31
Ni		4.4		12.4	26	3	5.1
Cu	1.7		24.1	39.8	6.1	5	4.1
Zn	3.5	94.9	8.3	929	81	28	12.1
As	0.039	10		4.24	1.4	1	0.7
Sr		11.1		7.39		6	2.6
Cd		1.5		3.13	1.4	13	0.6
Sb	0.23	4.6		3.69	1.6	0.4	0.25
La	0.12			0.49	0.28	0.2	0.23
Pb	0.45	23.8		175	20	11	1.97
Bi				0.8	0.18	0.04	0.02
Cl ⁺ *			0.525				1.9
NO ₃ ^{-*}			1.860		0.72		1.00
SO ₄ ^{2-*}			0.571		1.5		1.06
K ⁺ *					0.043		0.074 2
NH ₄ ⁺ *			0.0589		0.58		0.93
OC [*]			1.03				12.2
EC [*]			0.871				2.12

^a Clements et al., 2014 ^g Gaga et al., 2012 ^c Cheung et al., 2011 ^eKara et al., 2015 ^h Özlü, 2015 ⁱ Sağırh, 2013

* means $\mu\text{g.m}^{-3}$ _x means PM₁₀

Erdemli is a rural area in Turkey. The arithmetic mean concentrations of Ca, Ti, Fe, Ni and Zn were 3-7 lower than our values. However, the arithmetic mean concentration was 4 times larger than this study. Arithmetic mean of the anions and cations were similar with our findings except for Mg^{2+} and Cl^- . The concentrations of these ions were lower than that of this study.

The study made by Gaga et al. (2012) were also performed in Eskişehir. For comparison urban- traffic site concentration in PM_{10} in winter concentrations were used. All parameters were higher than our suburban sampling site.

The mean concentration of OC and in our study, was larger than the study done in Central Los Angeles ($PM_{2.5}$ and $PM_{2.5-10}$). Mean concentration of Cu in the study done by Cheung et al. (2011) was 6 times larger than our study. The mean concentrations of Mg, Al, Ca, Zn, Cl^- , SO_4^{2-} were lower than our study.

The study made by Kara et al. (2015) was performed in Aliğa, İzmir. The sampling site is highly industrialized. Arithmetic mean concentrations of Na, Mg, K, Ca, Mn, Fe, Pb, Bi were higher than our study. Arithmetic mean of Arsenic concentration was 8 times greater than our study whereas arithmetic mean of Sr concentrations was 3 times higher than our study.

This study is the third study performed in the same sampling site. The mean concentrations of Al, K, Ca, Co, Cu, Sr, Cd, Sb, Pb, and Bi in $PM_{2.5-10}$ and $PM_{2.5}$ were lower in this study. This decrease may be the result of natural gas use instead of coal and wood especially in the city center. The gradual decline in the concentration of Pb between 2009 and 2014 is mostly related with the usage of unleaded gasoline after 2000. The mean concentrations of NH_4^+ , Fe and Cr were larger in our study in two types of particles. The concentrations of NH_4^+ increased because of the extensive tendency in poultry industry. Furthermore, the arithmetic mean concentrations of SO_4^{2-} , EC and OC showed an increase in only $PM_{2.5}$ in this study.

4.9 Sources apportionment

4.9.1 Crustal enrichment factor

Enrichment factors (EFs) of for both fractions ($PM_{2.5}$ ve $PM_{2.5-10}$) were calculated for indicating the relative contribution of natural and anthropogenic sources and results were shown in Figure 4.22. Crustal element Sm was used as a reference element in EFC calculation. The result of the calculation was drawn in logarithmic scale and 1-10 signs crustal origins of elements and 10-100 values sign enriched elements and 100 and higher than 100 values sign as highly enriched elements (Shridhar et al. 2010). In $PM_{2.5}$, Se, Sb, As, Cd, Hg, Pb, Cr, Sn, Mo, Zn, Ni, Ge, Sc, Ca, Cs, Ba, Mg, Al, Na have the enrichment factor higher than 10 whereas the enrichment factors of Se, Sb, Hg, Cr, Cd, Mo, Zn, Sn, As, Pb, W, Ni, Cu, Sc, Ca, Ge, Ba are higher than 10 in $PM_{2.5-10}$.

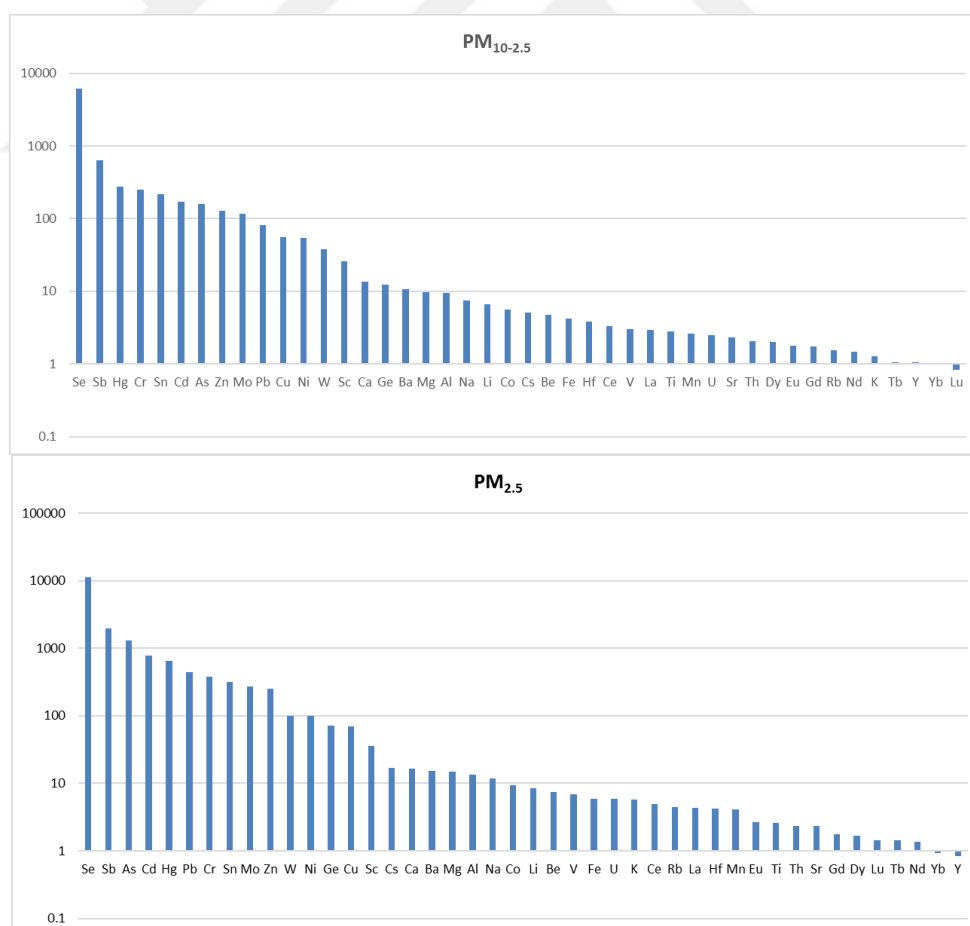


Figure 4.22. Enrichment factors for $PM_{2.5}$ and $PM_{2.5-10}$

4.9.2 Wind sector analysis

The concentrations of particulate matter at a specific location mostly depend on the local sources and meteorological variables. Therefore, possible pollution sources must be found before the investigation of aerosol data. Our sampling station was not under direct influence of local emissions.

Firstly, wind rose was prepared for the whole sampling period. Wind directions were associated with wind speed for each hour. The wind rose is shown in Figure 4.23. The dominant wind direction is WSW direction. 19.1% of total wind was categorized as calm.

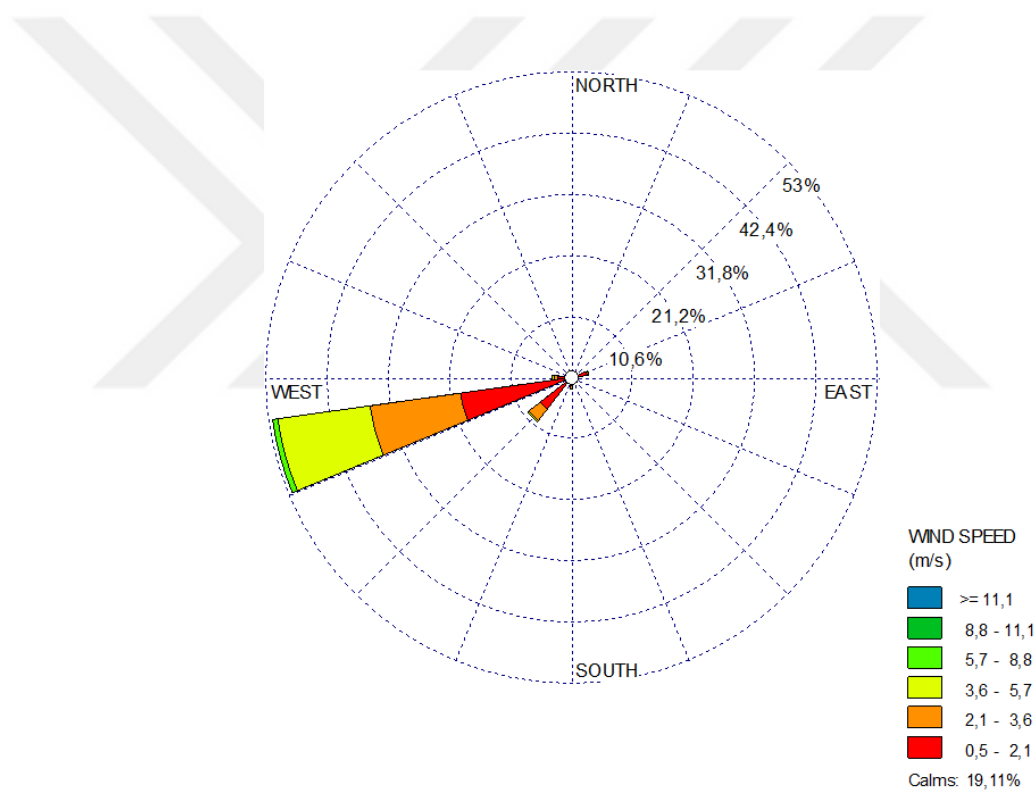


Figure 4.23. Annual wind rose

Monthly variations of wind sectors were drawn and shown in Figure 4.24. Wind from West South West (WSW) sector was the most dominant one in all months. Wind from the South, East South East (ENE) had effects in March 2013. In October, November, December, January and February, not only wind from WSW sector but also SSE and ENE sectors had effects on samples collected.

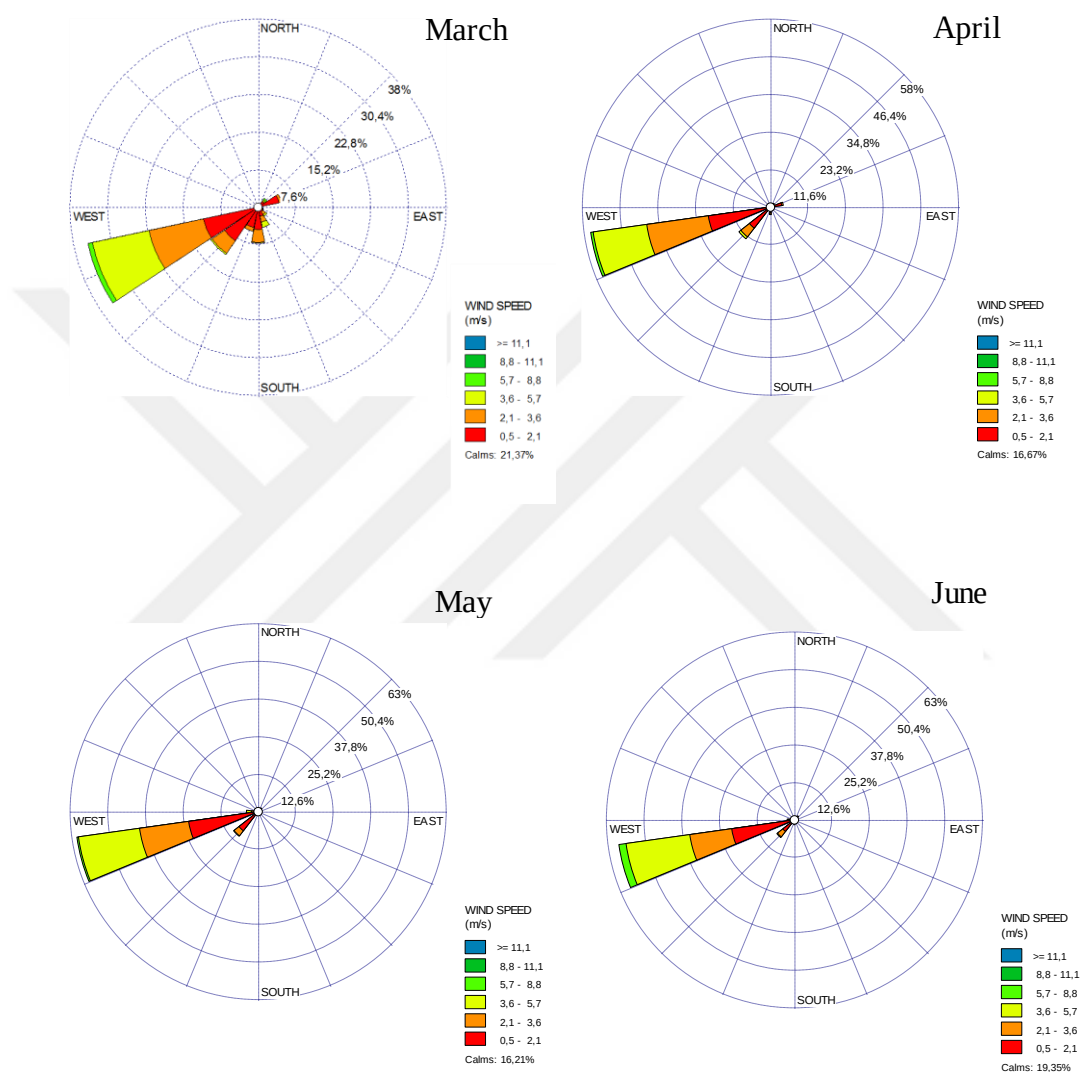
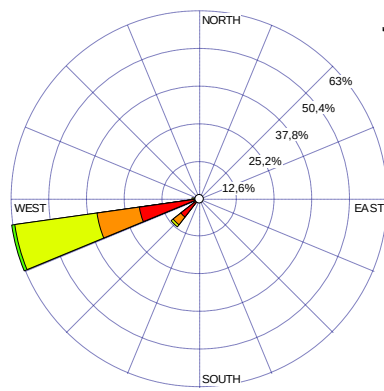
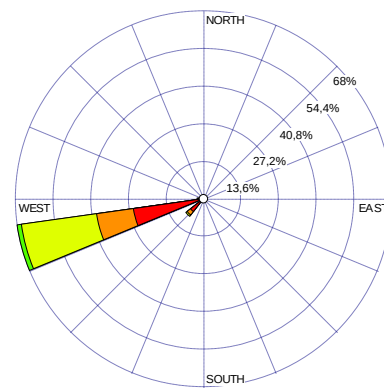
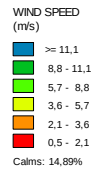


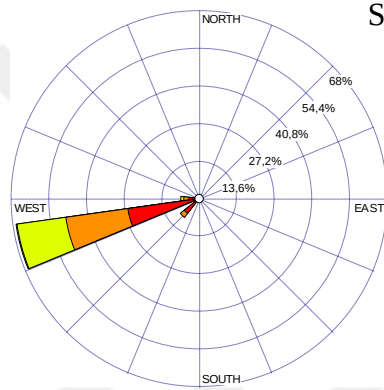
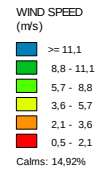
Figure 4.24. Monthly wind roses



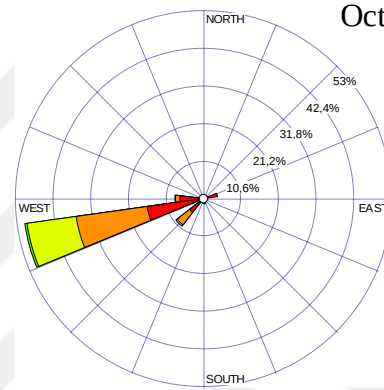
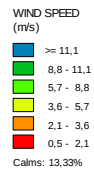
July



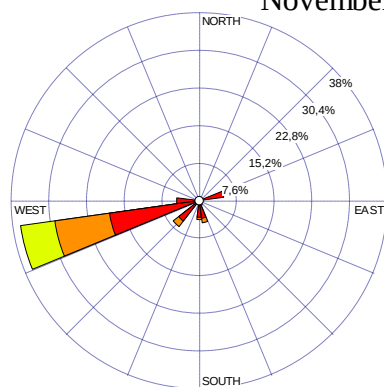
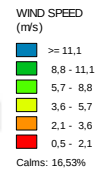
August



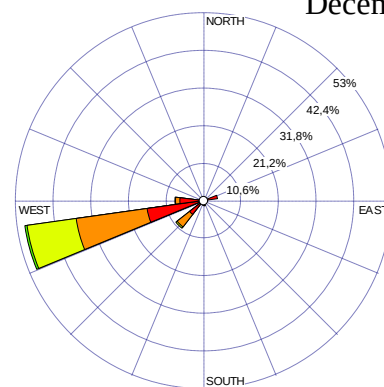
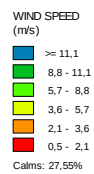
September



October



November



December

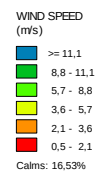


Figure 4.24. Monthly wind roses (continued)

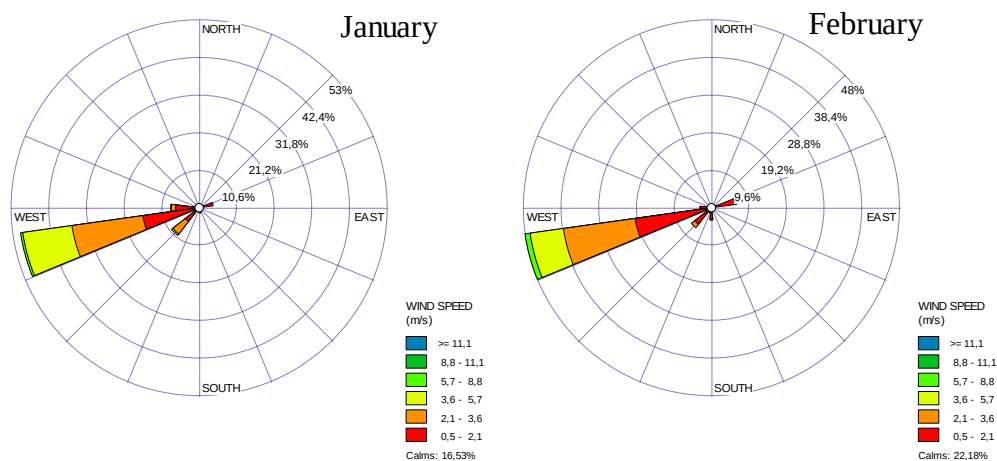


Figure 4.24. Monthly wind roses (continued)

Pollution roses for $PM_{2.5}$ were illustrated in Figure 4.25. In $PM_{2.5}$, high concentrations of crustal elements like titanium, Sr, Ti, Y, Mn, La, Nd, Ce, Pr, Eu, Sm, Gd, Dy, Er, Th, U were mostly observed in South (S) direction. It can be related with the agricultural areas in S direction of the sampling points. Elements related with sea like Na, Ca, Mg showed similar wind sector, WSW. Aluminum, Mg, Na, K, Sc, Ca, V, Cr, Fe, Co, Ba showed similar frequent wind sectors, W, WSW, S, ESE, ENE. These elements can be affected by forests, agricultural areas, and residential areas. The dominant wind sectors of anthropogenic elements like Ni, Hg, Sn, Cd, Se, Mo, Sb, Tl, Bi, Pb, Ge, Rb, As, Zn, Cu were from E, ESE, and ENE. These sectors indicated residential areas located especially in the city center (Table 1.3).

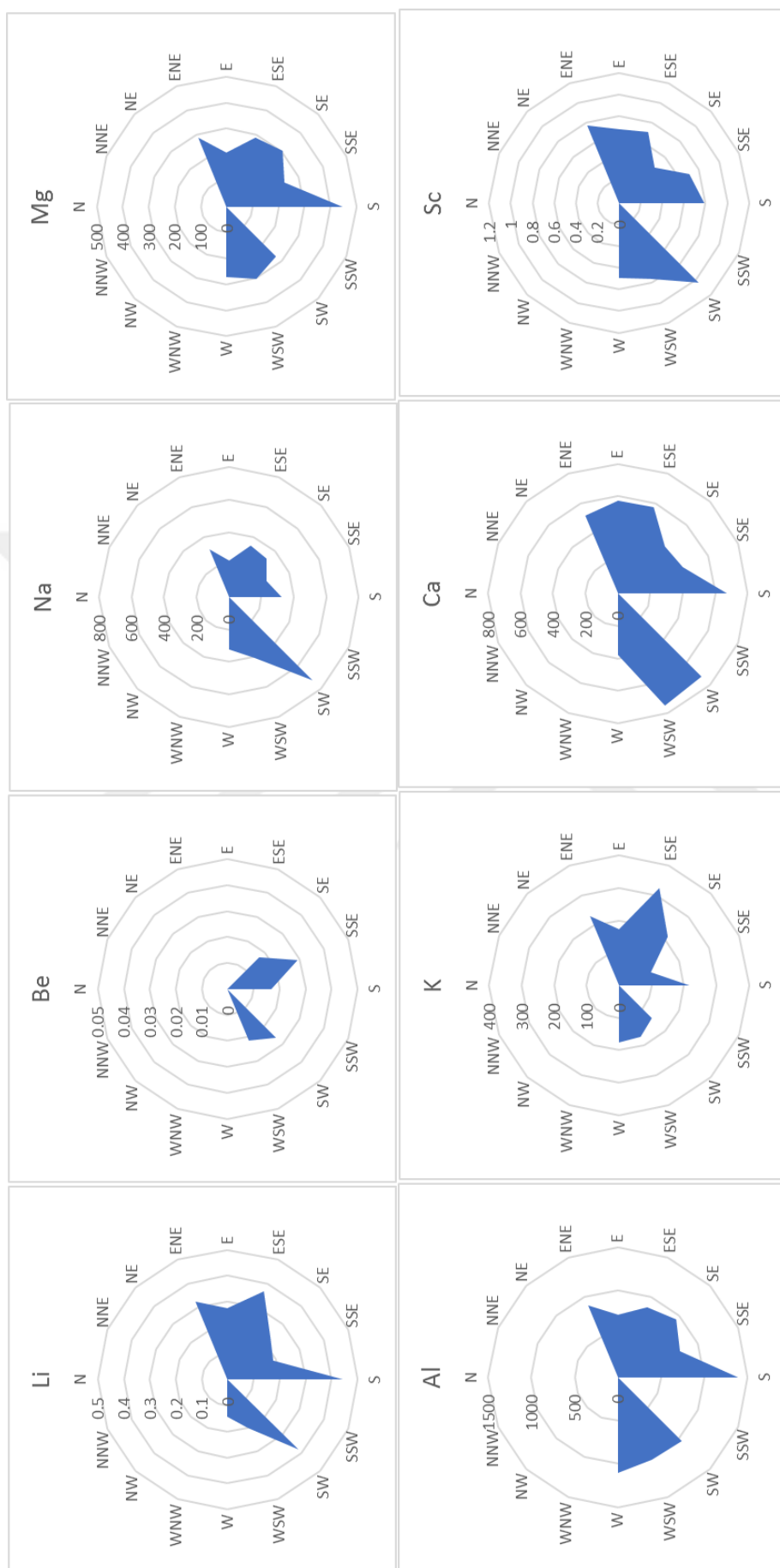


Figure 4.25. The pollution roses in PM_{2.5}

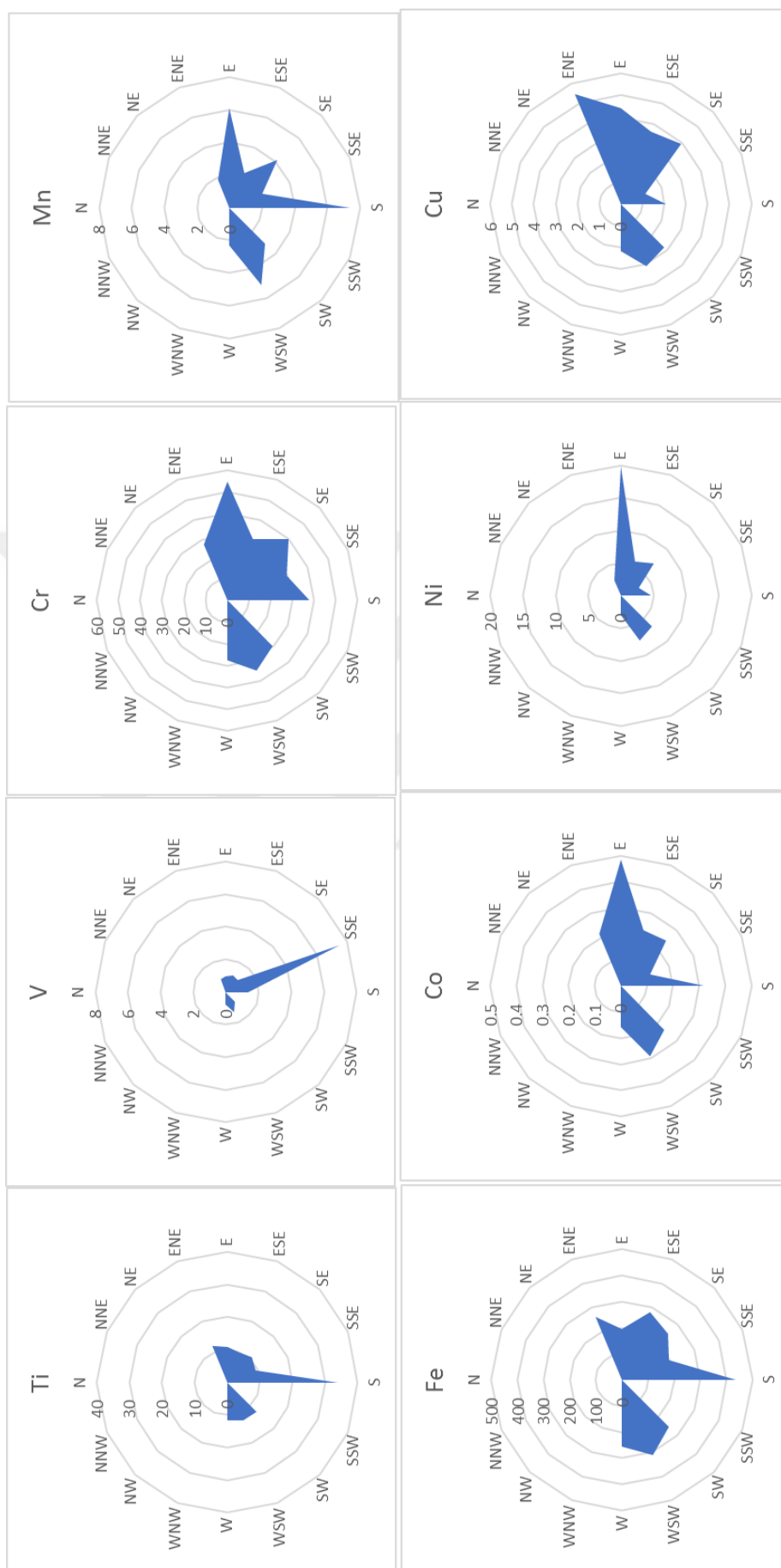


Figure 4.25. The pollution roses in PM_{2.5} samples (continued)

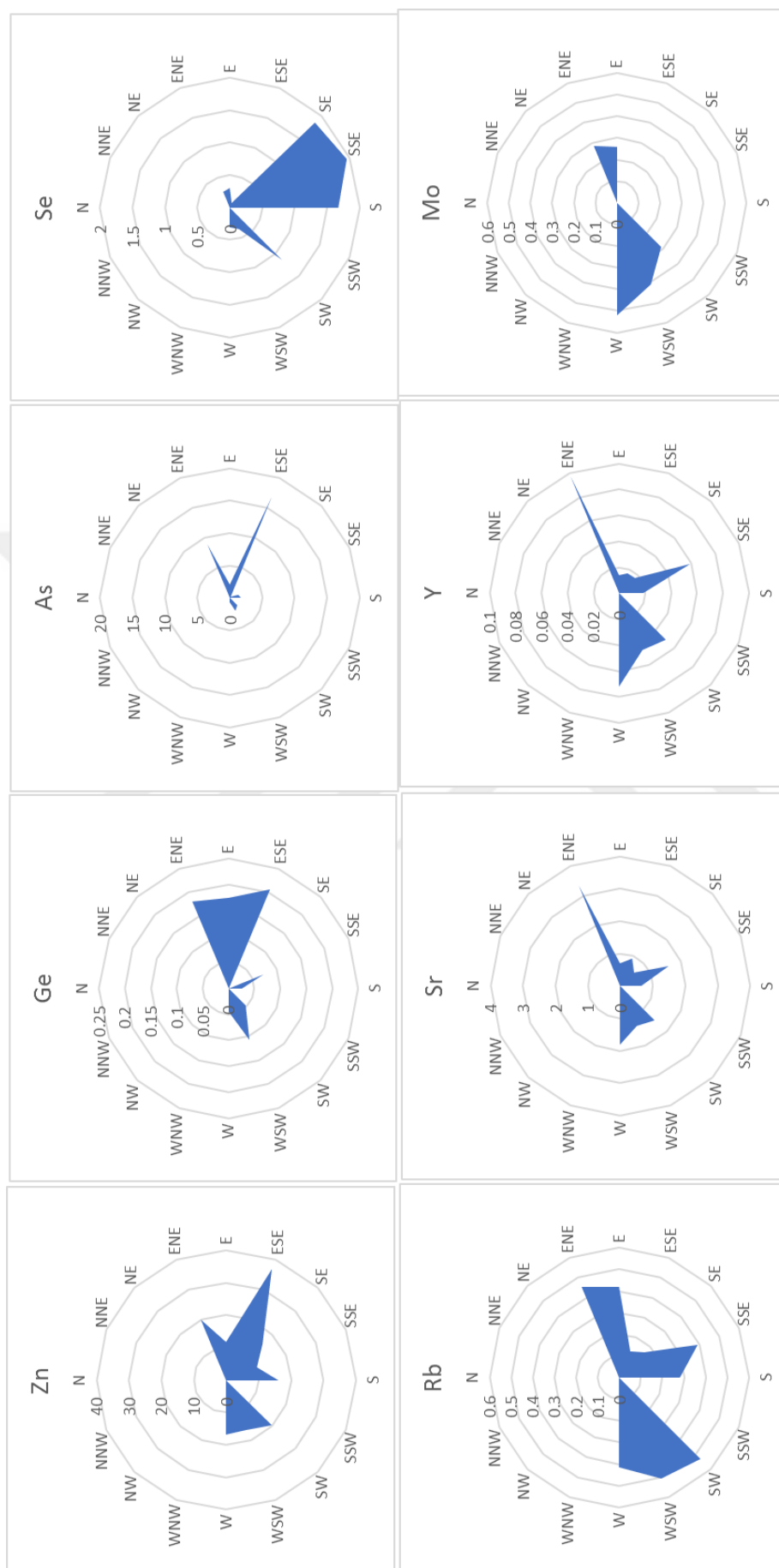


Figure 4.25. The pollution roses in $PM_{2.5}$ samples (continued)

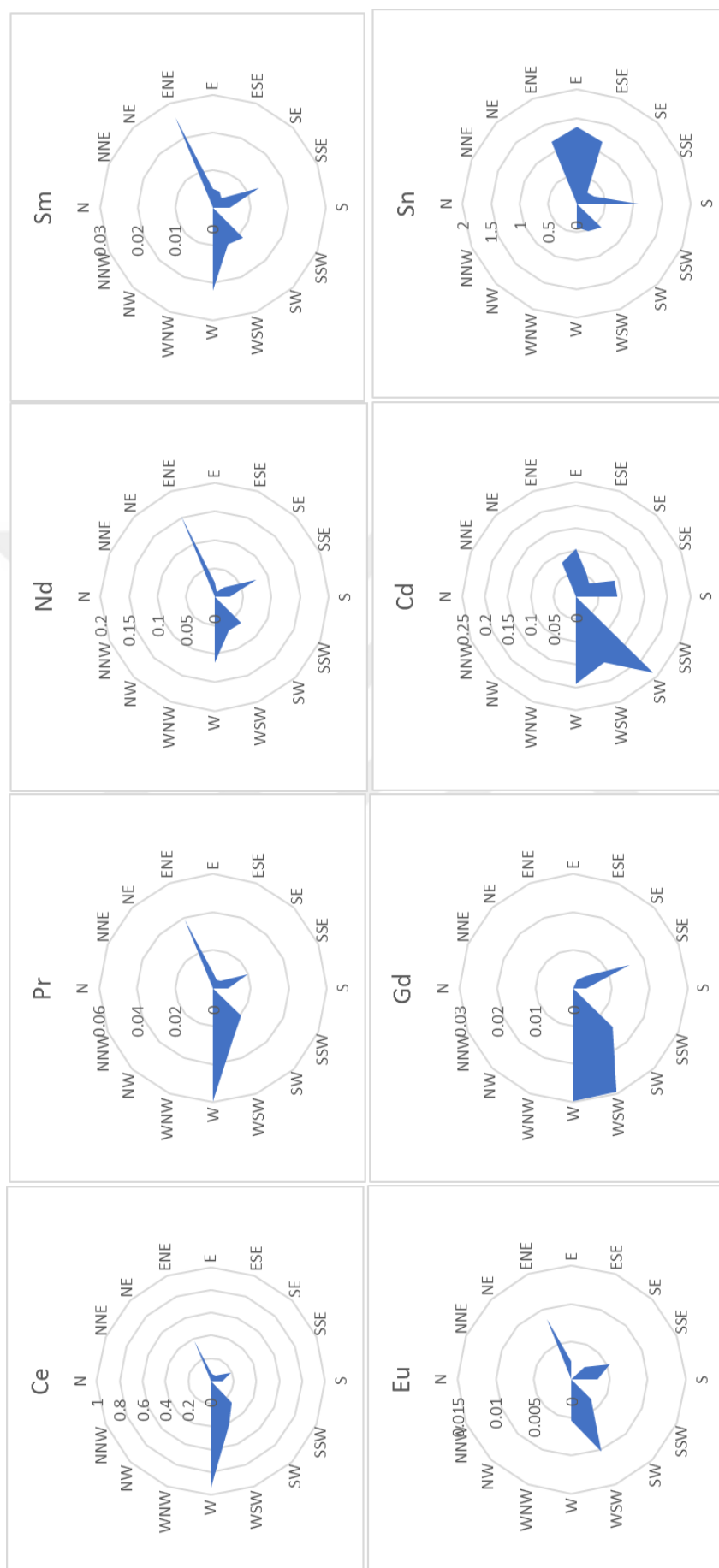


Figure 4.25. The pollution roses in $PM_{2.5}$ samples (continued)

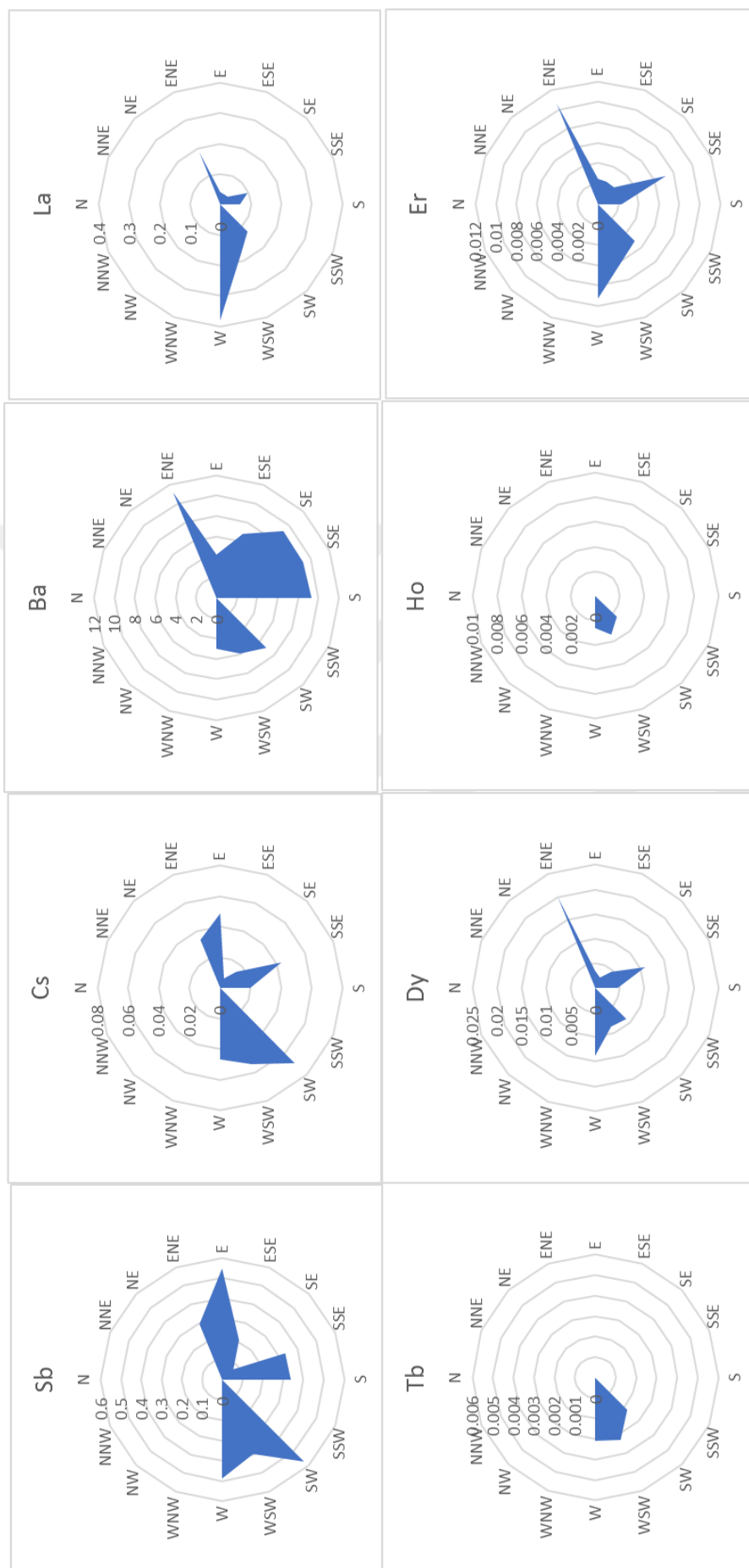


Figure 4.25. Pollution roses in PM_{2.5} samples (continued)

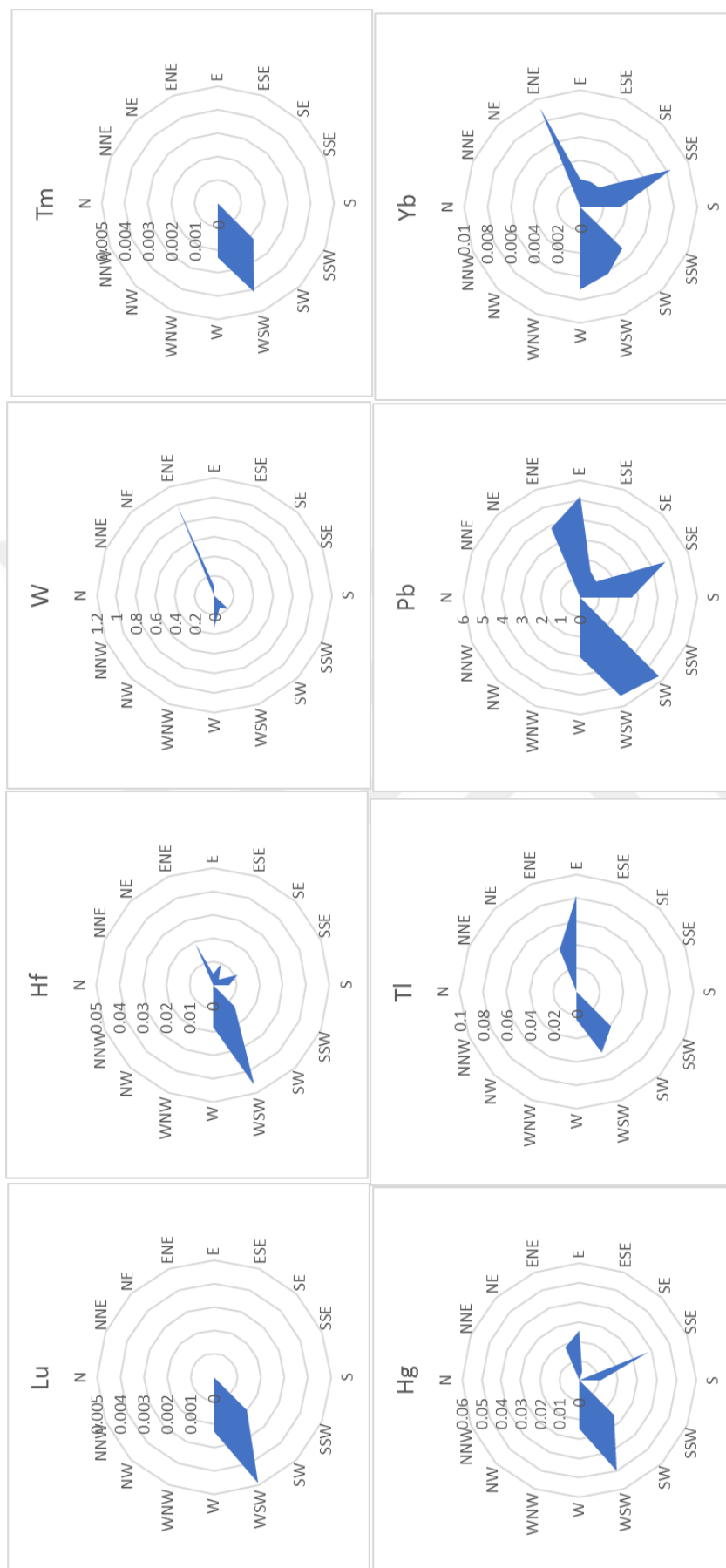


Figure 4.25. Pollution roses in PM_{2.5} samples (continued)

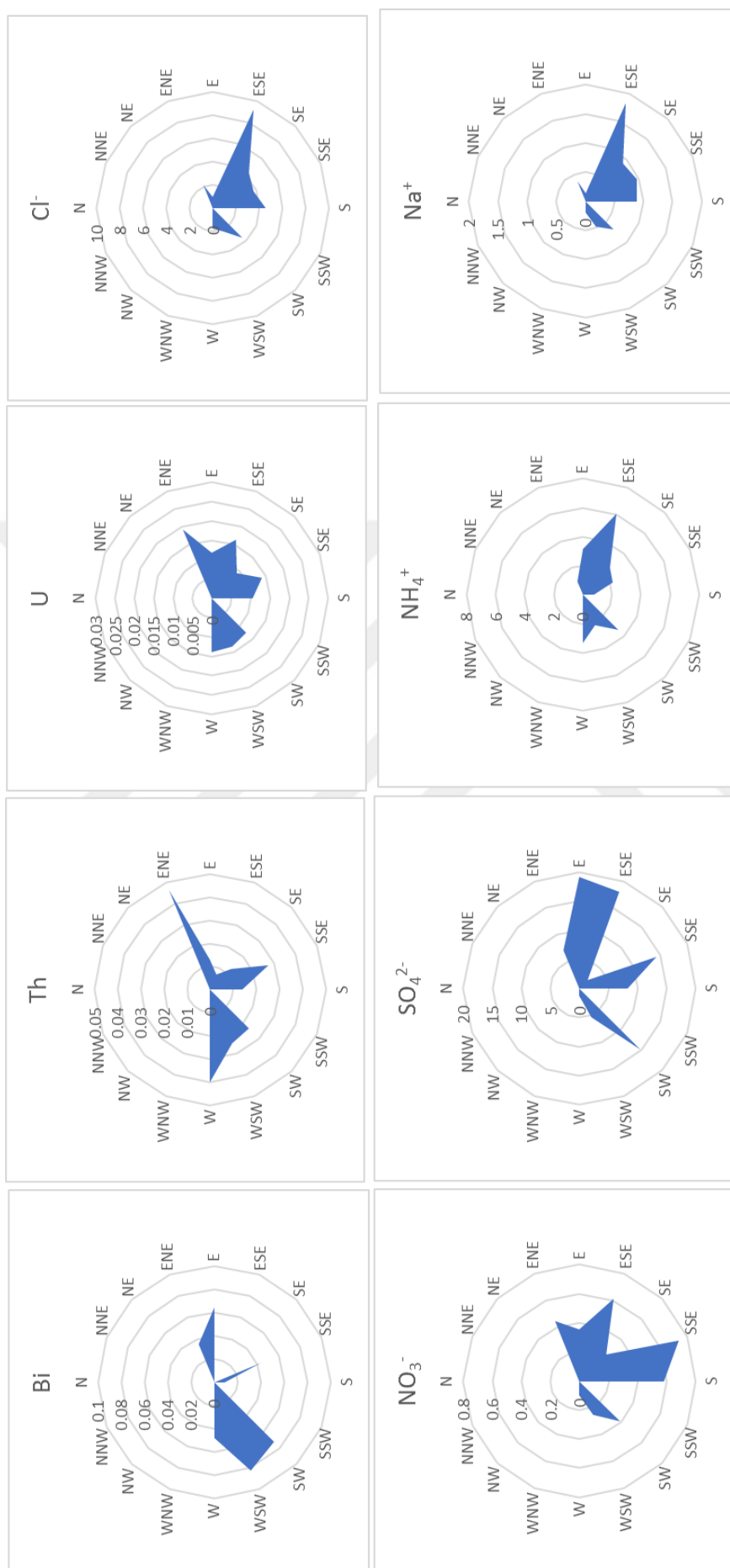


Figure 4.25. Pollution roses in PM_{2.5} samples (continued)

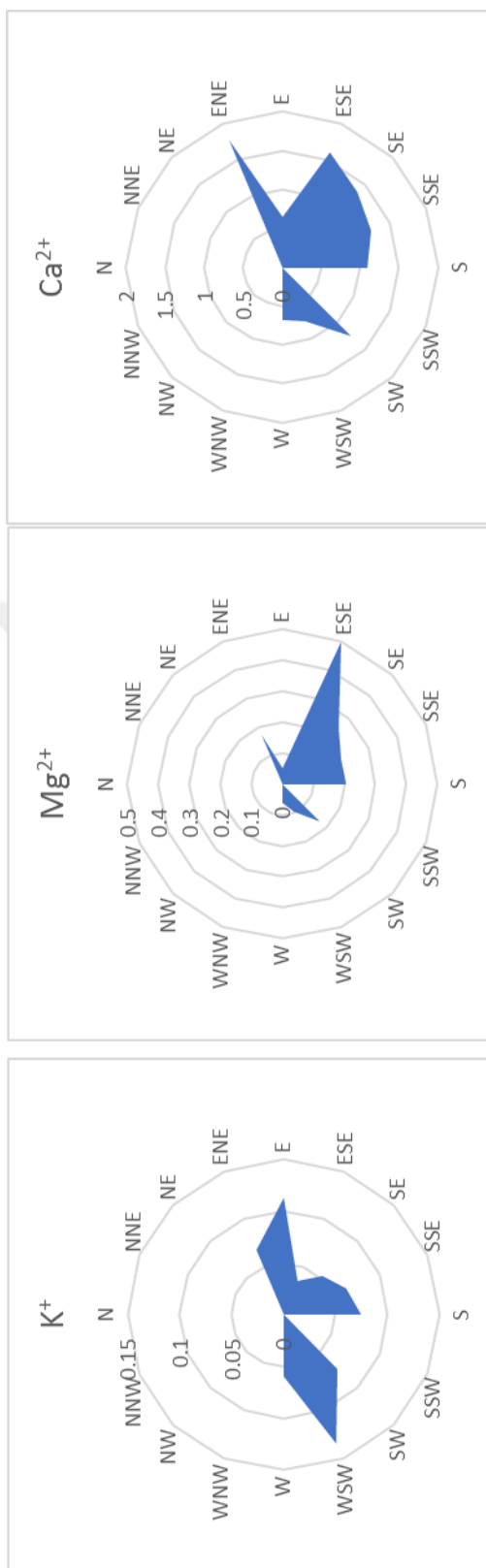


Figure 4.25. Pollution roses in $PM_{2.5}$ samples (continued)

Pollution roses for PM_{2.5-10} samples were illustrated in Figure 4.26. For antropogenic elements like Cu, Zn, Ge, As, Se, Mo, Cd, Sn, Sb, Tl, Pb, Bi winds from ESE and ENE were dominant. For other elements, the most frequently wind sector was S direction. These indicate residential areas and agricultural areas (Table 1.3).



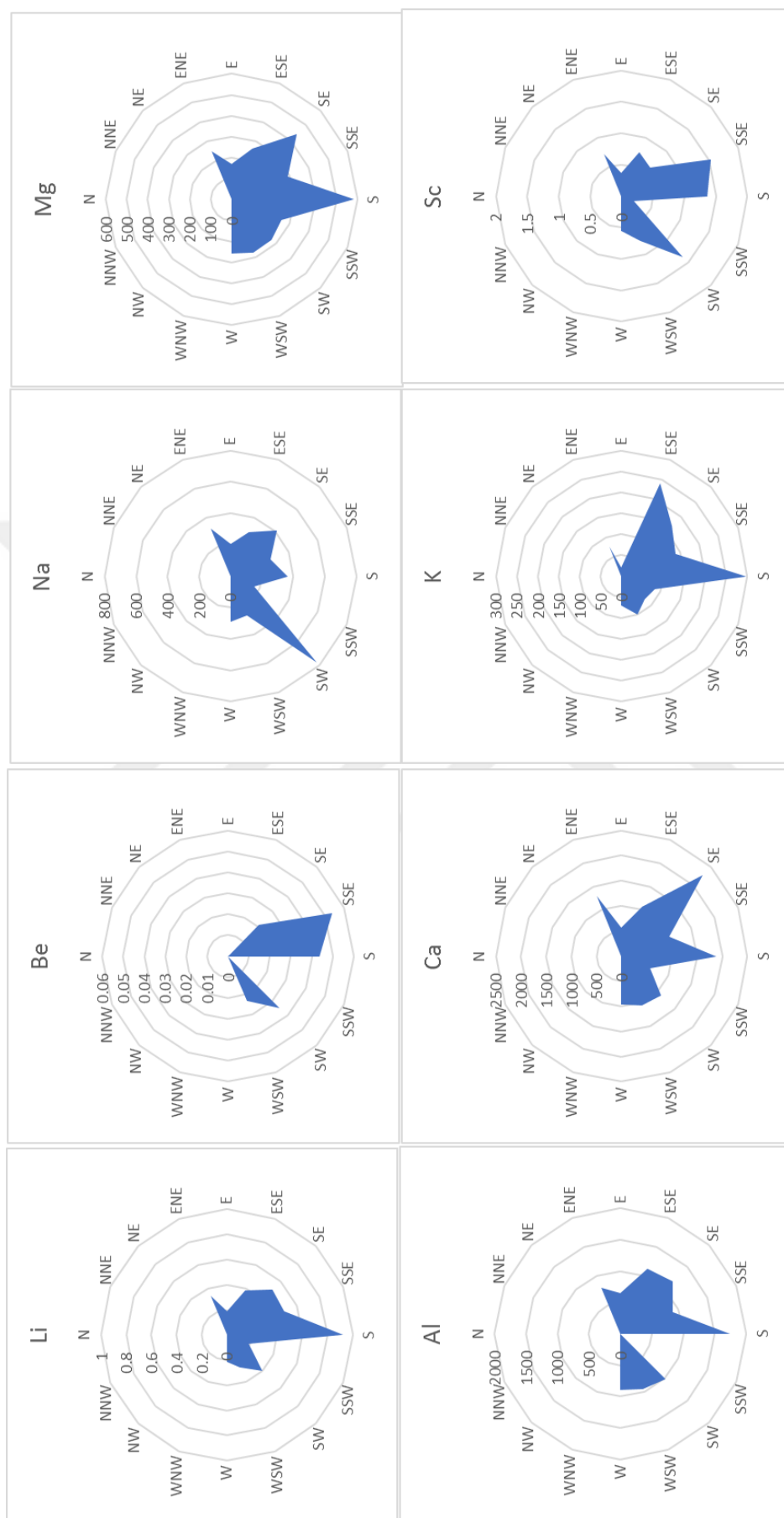


Figure 4.26. The pollution roses of $PM_{10-2.5}$ samples

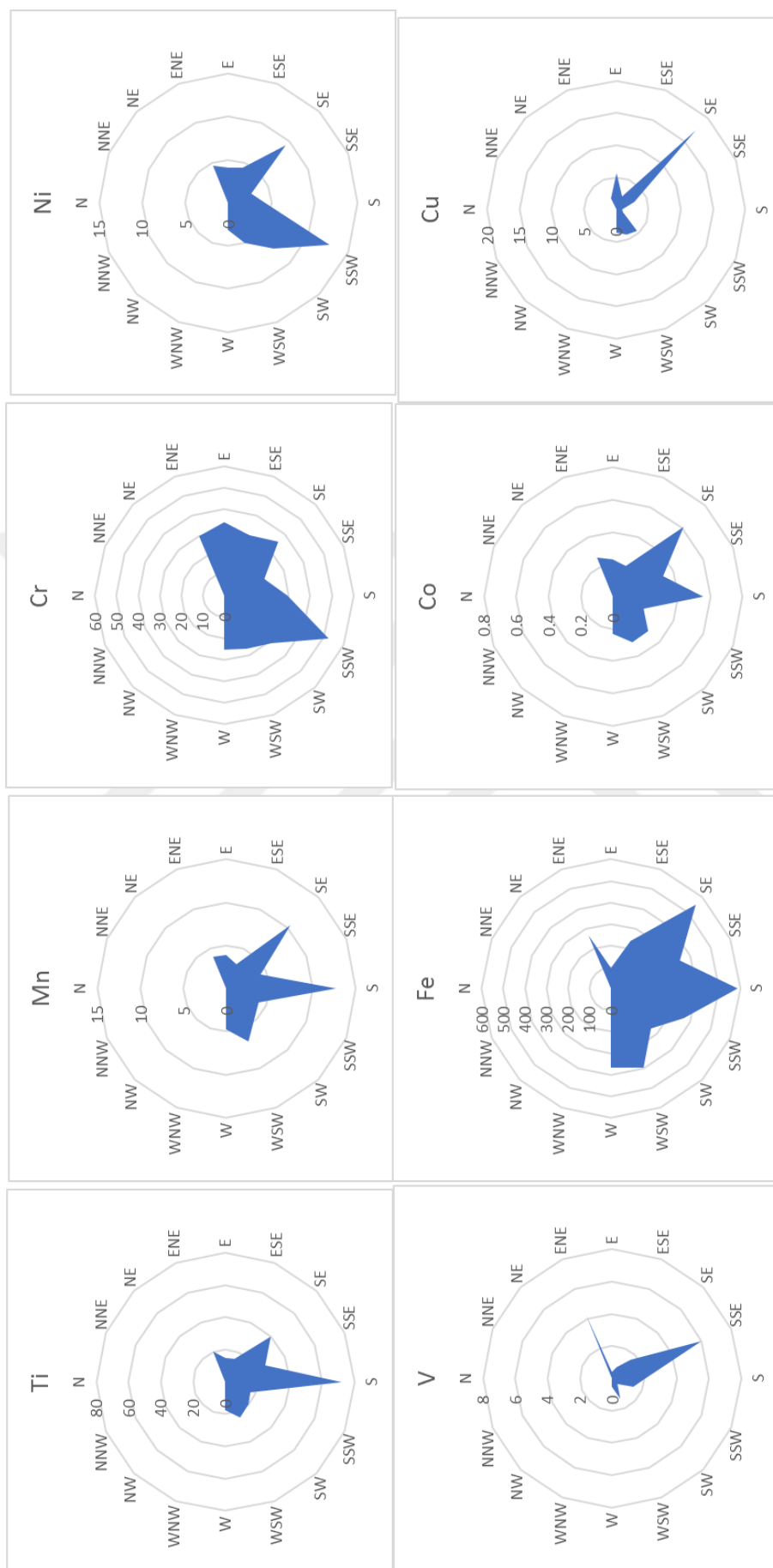


Figure 4.26. The pollution roses of PM_{10-2.5} samples (continued)

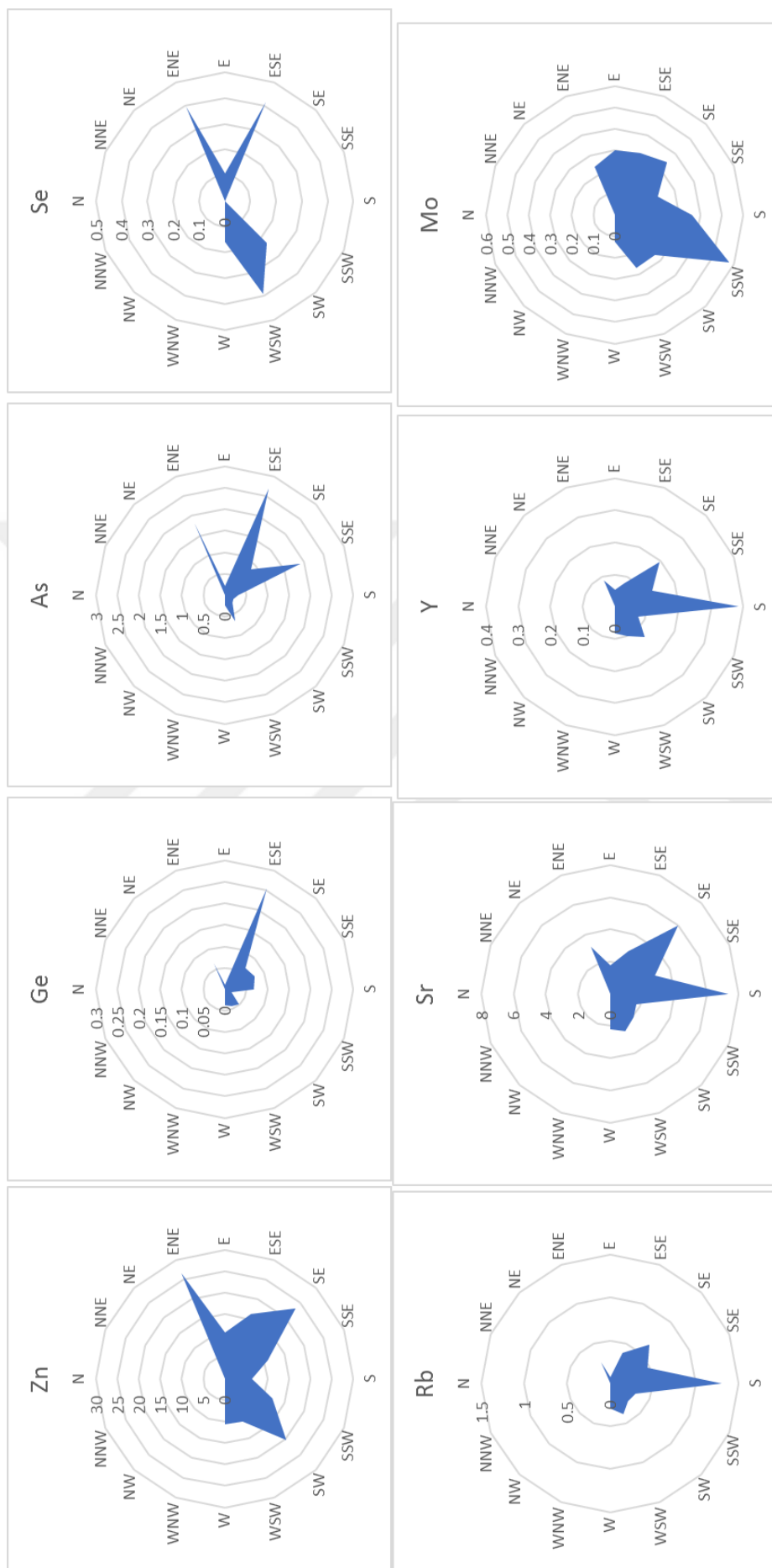


Figure 4.26. The pollution roses of $PM_{10-2.5}$ samples (continued)

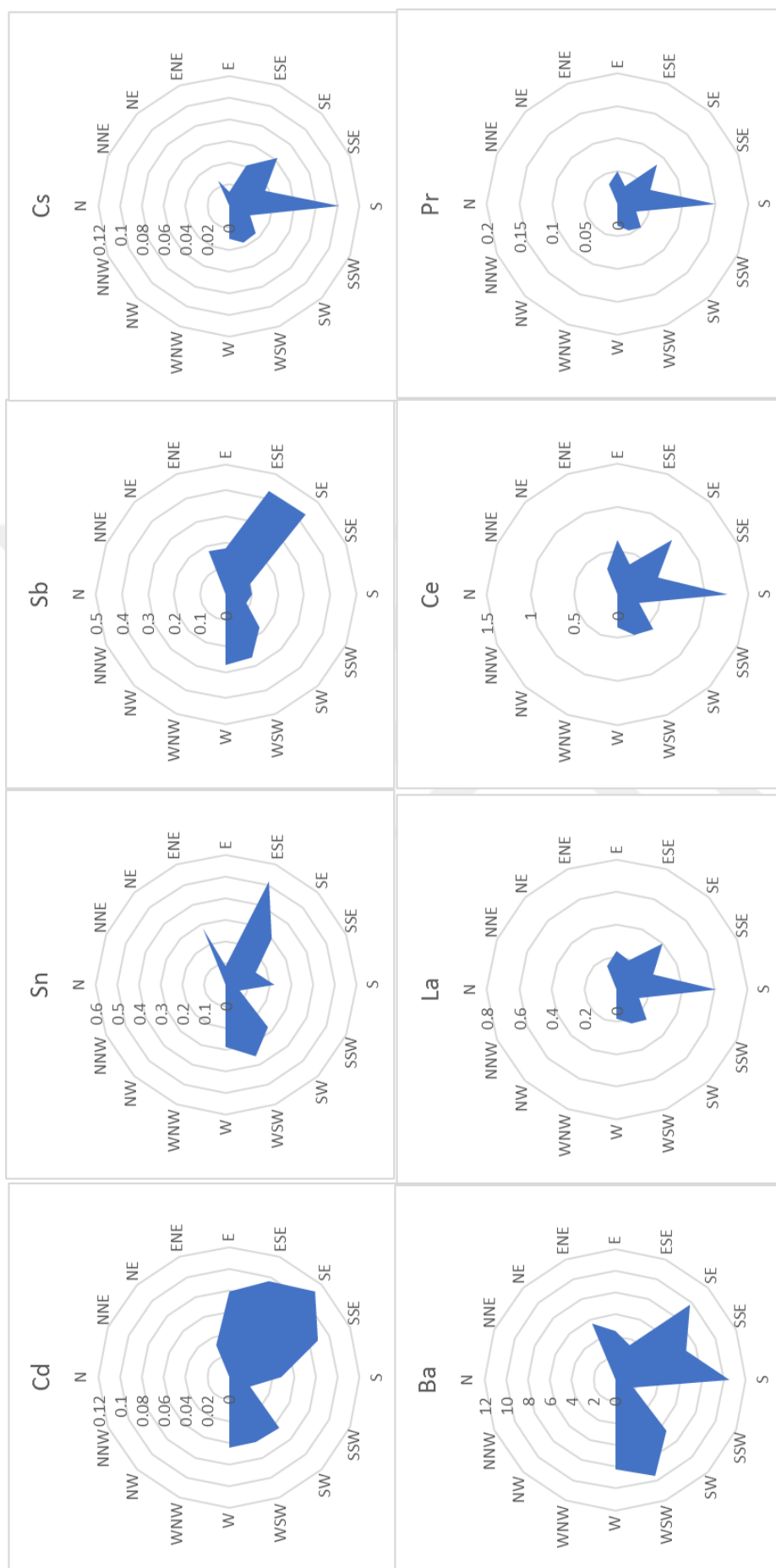


Figure 4.26. The pollution roses of $PM_{10-2.5}$ samples (continued)

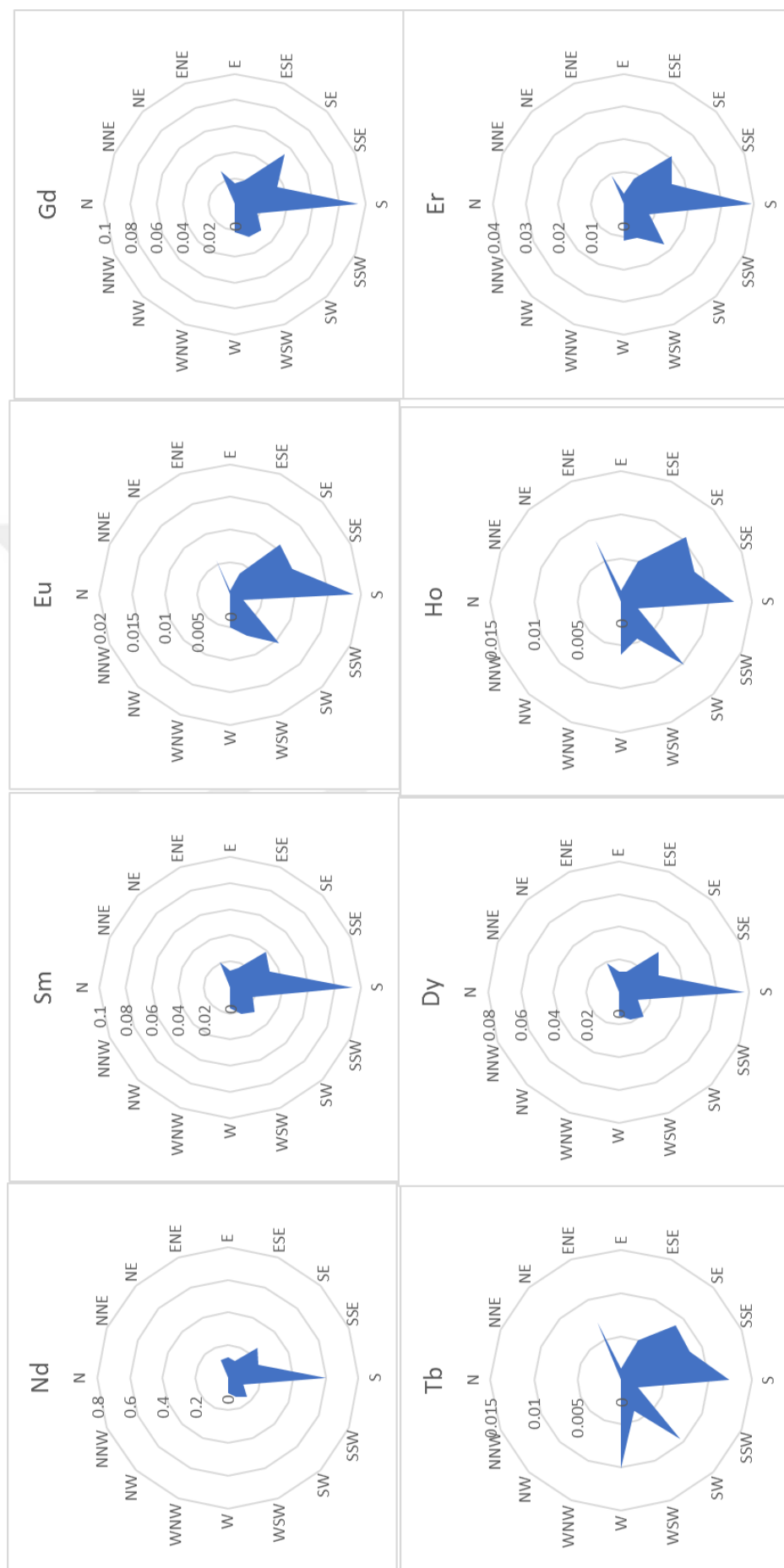


Figure 4.26. The pollution roses of $PM_{10-2.5}$ samples (continued)

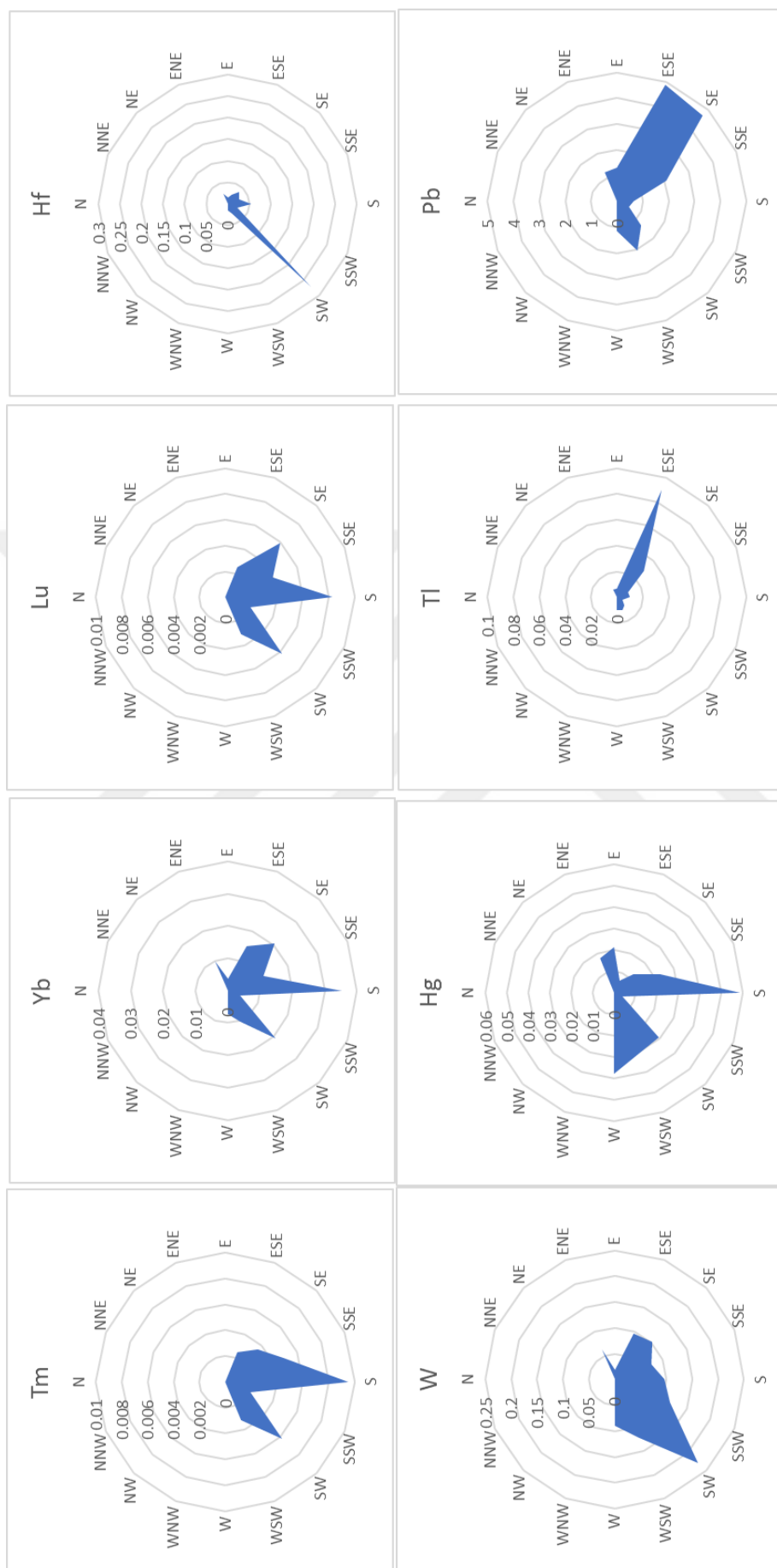


Figure 4.26. The pollution roses of PM_{10-2.5} samples (continued)

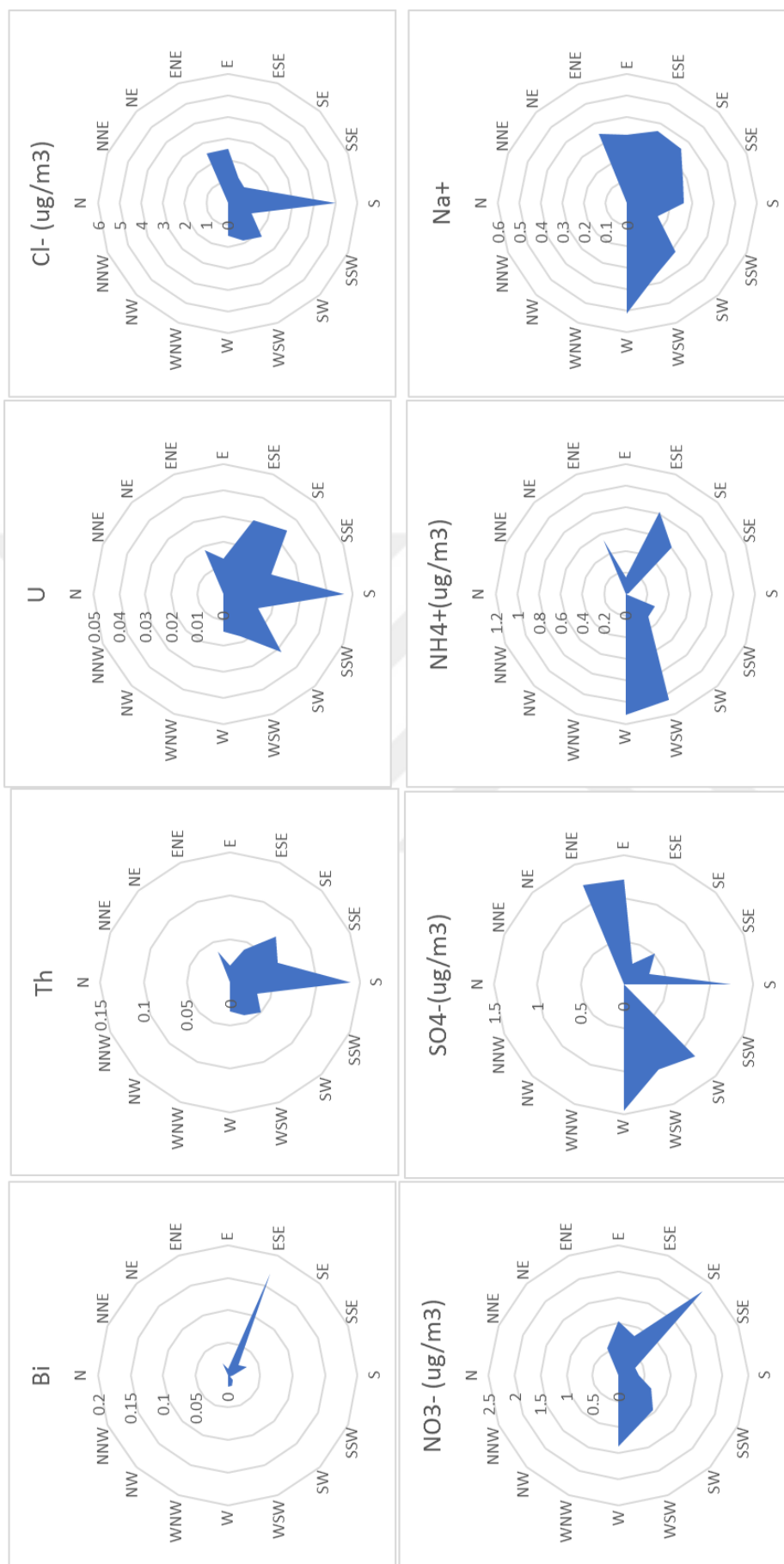


Figure 4.26. The pollution roses of $\text{PM}_{10-2.5}$ samples (continued)

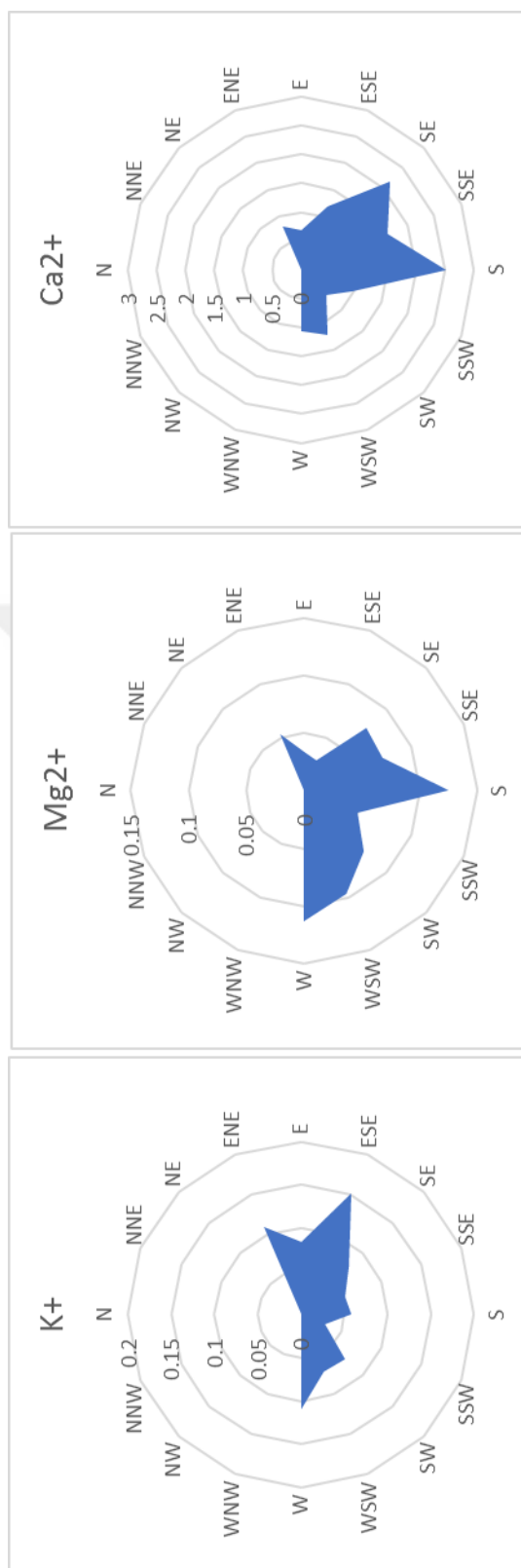


Figure 4.26. The pollution roses of PM_{10-2.5} samples (continued)

4.9.3 Positive matrix factorization studies

4.9.3.1 Positive matrix factorization results for PM_{2.5-10}

After the preparation of concentration and uncertainty file, the signal to noise ratio was categorized as bad if the ratio is less than 0.5, as ‘Weak’ if the S/N ratio is between 0.5 and 1 and ‘Strong’ greater than 1. Secondly, the outliers were discarded from the concentration time series graphics. And then the base model results were evaluated. Base model screen gave Q_{robust} and Q_{true} values. Q_{robust} must be 10% greater than the Q_{true} -value (Norris and Harrison, 2014). Q_{theoric} value was calculated by the equation

$$Q_{\text{theoric}} = \frac{n \cdot m}{n + m - p}$$

where n is the number of species (weak and strong), m is the number of samples in the data set, and p is the number of factors fitted by the model. Q_{robust} and Q_{true} values must be at most 1.5 times Q_{theoric} value. The base model was rerun until obtaining the required values of Q_s by excluding outliers, making some of the species as weak and increasing the number of factors etc. The Q values were shown in Table 4.10. Then observed and predicted time series screen was used to evaluate the fitting of the model for each species. As a result, the r^2 values was checked and some species categories change to weak. Lastly, Ca, Sc, V, Cr, Fe, Ni, Cu, Zn, As, Mo, Cd, Ba, Eu, W, Hg, Pb, Bi, Cl⁻, NO₃⁻, SO₄²⁻, and NH₄⁺ categorize as ‘Weak’ and Be, Sn, Se, Ge, Tb, Ho, Tm, Lu, Na⁺, K⁺, Mg²⁺, and Ca²⁺ was selected as ‘Bad’. After that studies, factor profiles (using concentration species and a percent of total factor) and G-scores were obtained. Factor profiles showed the factor contribution in each species as a concentration and a percent contribution. The combination with the daily wind sectors, a graph was also obtained.

Table 4.10. The base model results of PM_{2.5-10}

Factor Number	$Q_{\text{theoretical}}$	Q_{true}	Q_{robust}	$Q_{\text{robust}}/Q_{\text{theoretical}}$	$Q_{\text{true}}/Q_{\text{robust}}$
8	9376	13201	12654	1.34	1.04

The relationship between the factors was evaluated by using the correlations of factors with each other (Figure 4.27). It is a way to investigate the rotational ambiguity between factors. The low r^2 values showed that there is no significant relationship between factors except for the relationship between Factor 5 and Factor 7. Factor 5 explained the soil factor. On the other hand, Factor 7 was identified as road dust contributions. Road dust factor was normally affected by the soil. The PMF version 5.0 programme also searches the rotational ambiguity in a solution. The model produces lots of $dQ_{\max}$. However, interpretation was done by using the results for the 4., 8., 15., and 25. solutions of problem. There are 4 outputs after running (Norris and Harrsison, 2014). The results of solutions our PMF studies for $PM_{2.5-10}$ were shown below:

			0	0			
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0

The output shows the error with numbers. While 0 present no error, 6 or 9 shows that the run was aborted. The first value must be 0. Otherwise the DISP results will be invalid. DISP Error Estimation can be run without running BS or can be run after BS and BS-DISP (Norris and Harrison, 2014).

The predicted total concentrations by PMF for each parameter were compared with the median values of the parameter which is uploaded to the programme (Table 4.11). The ratios were close to unity except for NH_4^+ . Therefore, the predicted concentrations were similar with the observed concentrations.

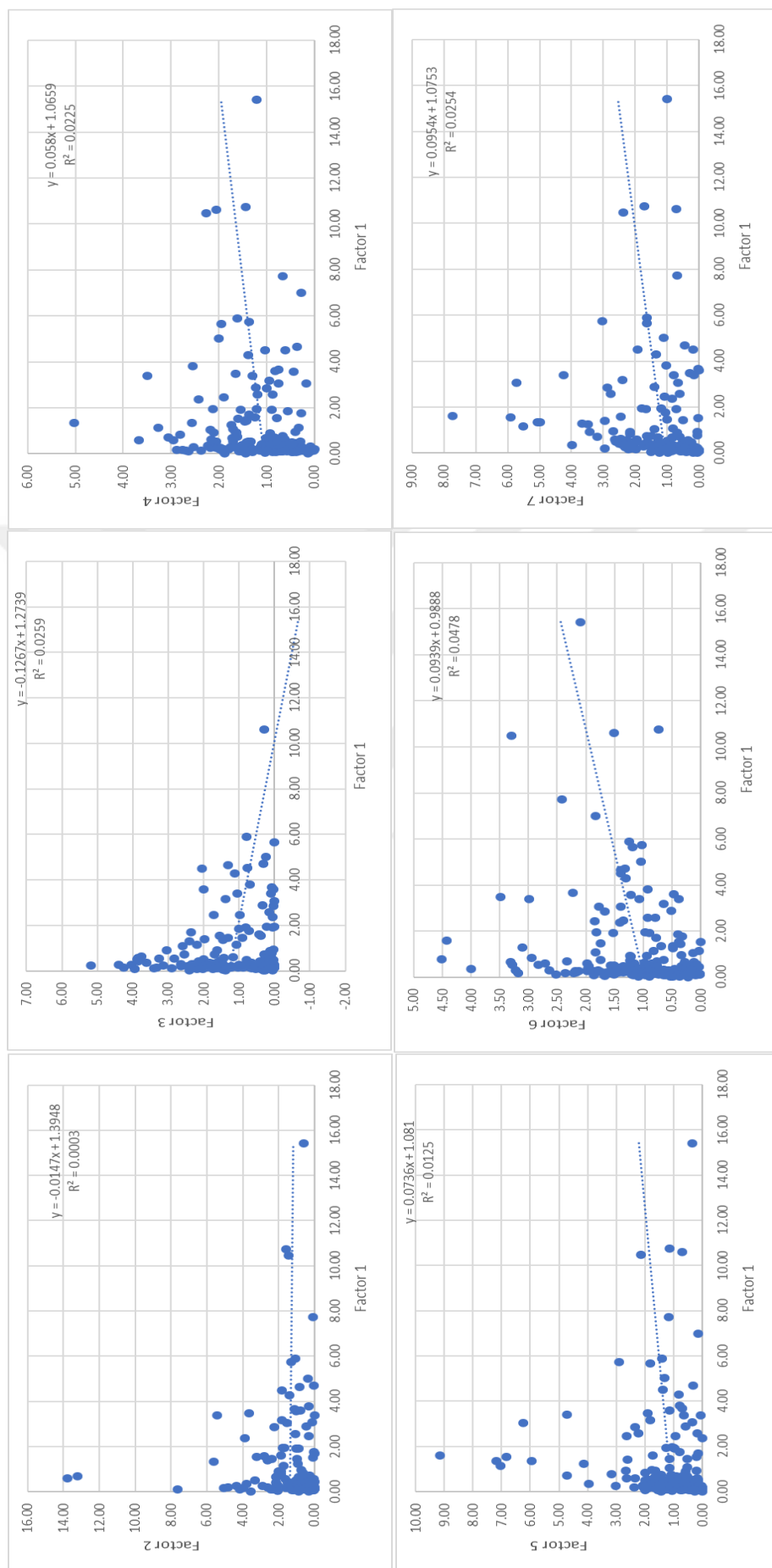


Figure 4.27. G space plots of factors for the PM_{2.5-10} analysis

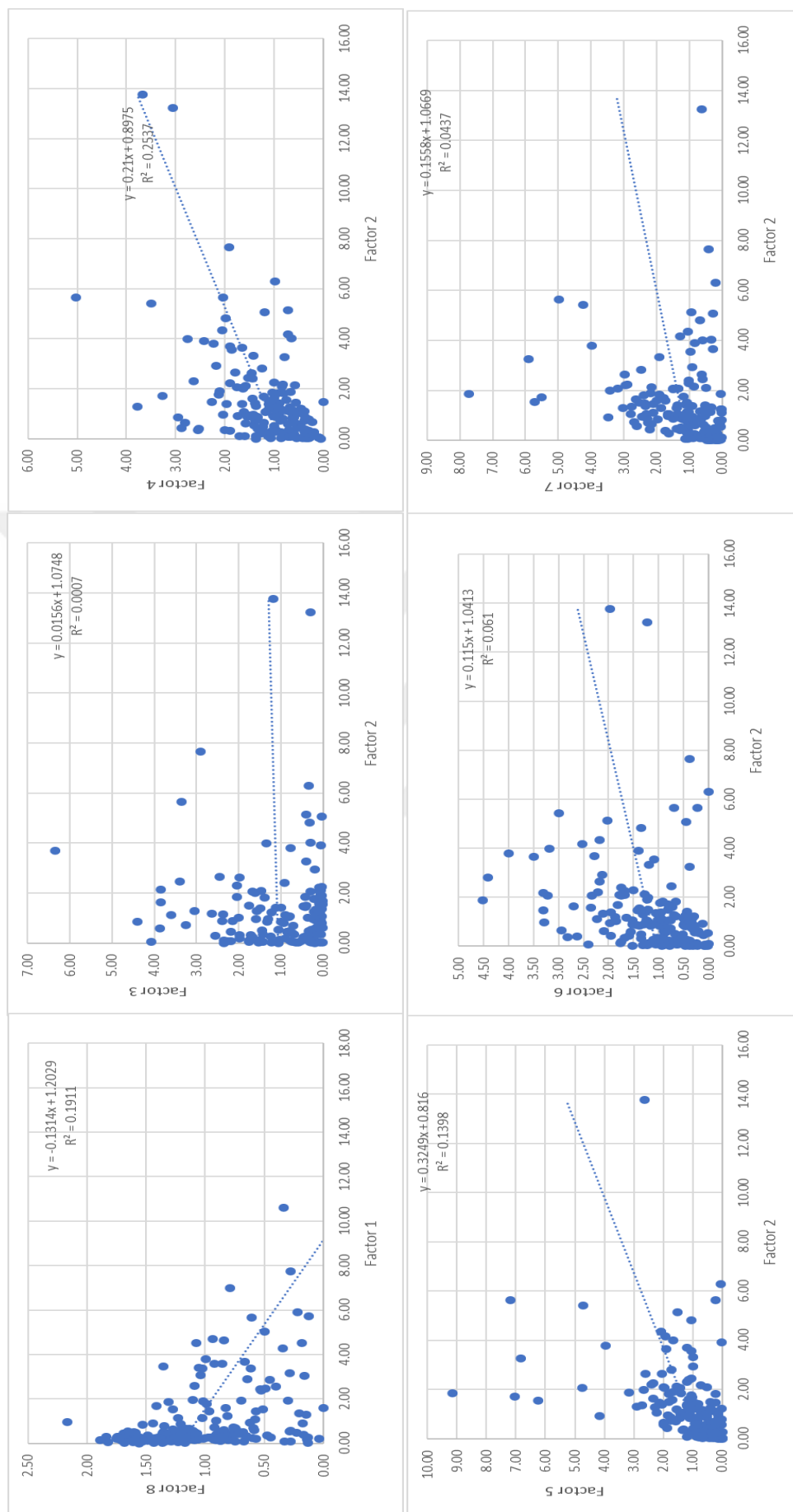


Figure 4.27. G space plots of factors for the PM_{2.5-10} analysis(continued)

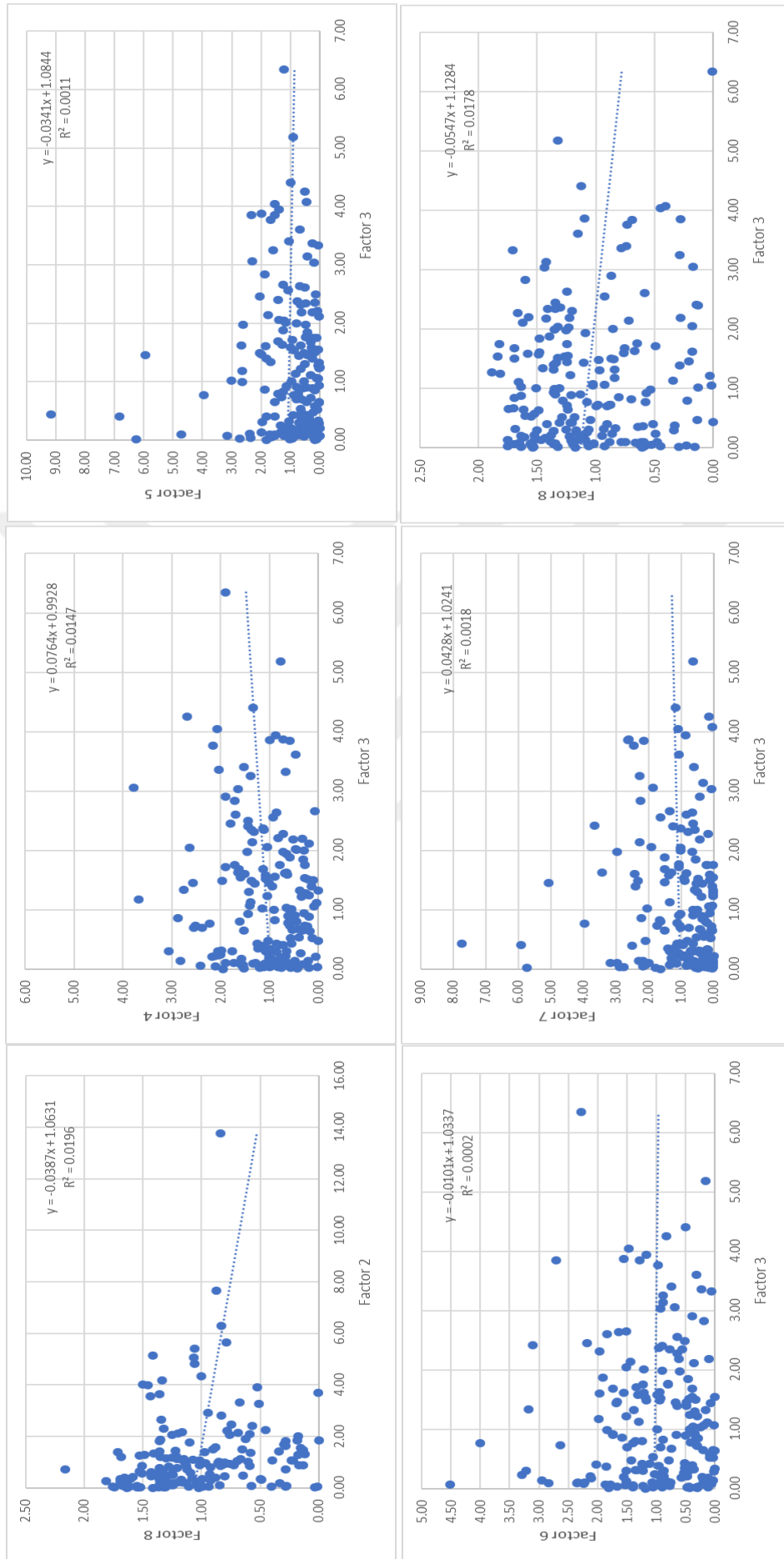


Figure 4.27. G space plots of factors for the PM_{2.5-10} analysis (continued)

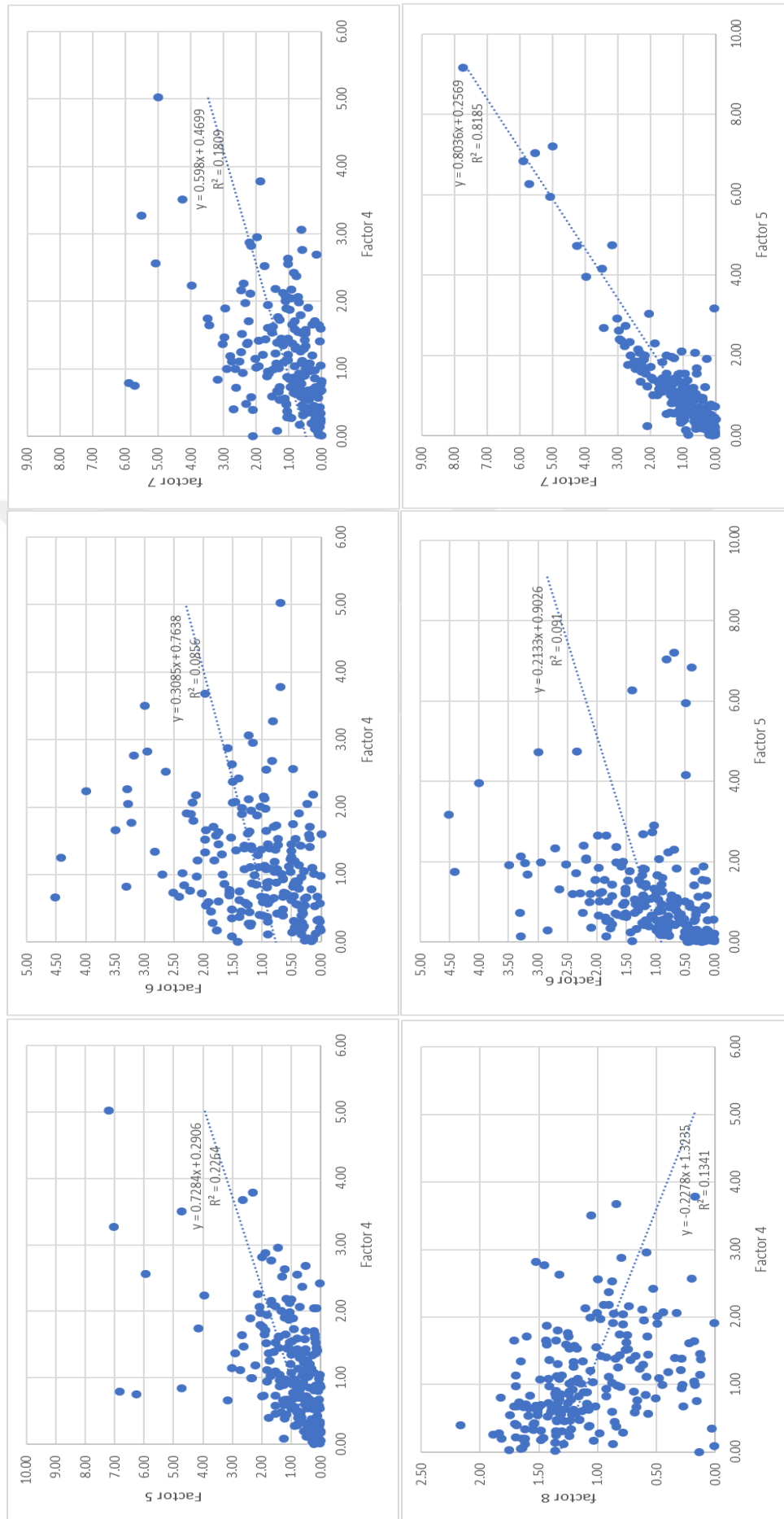


Figure 4.27. G space plots of factors for the PM_{2.5-10} analysis (continued)

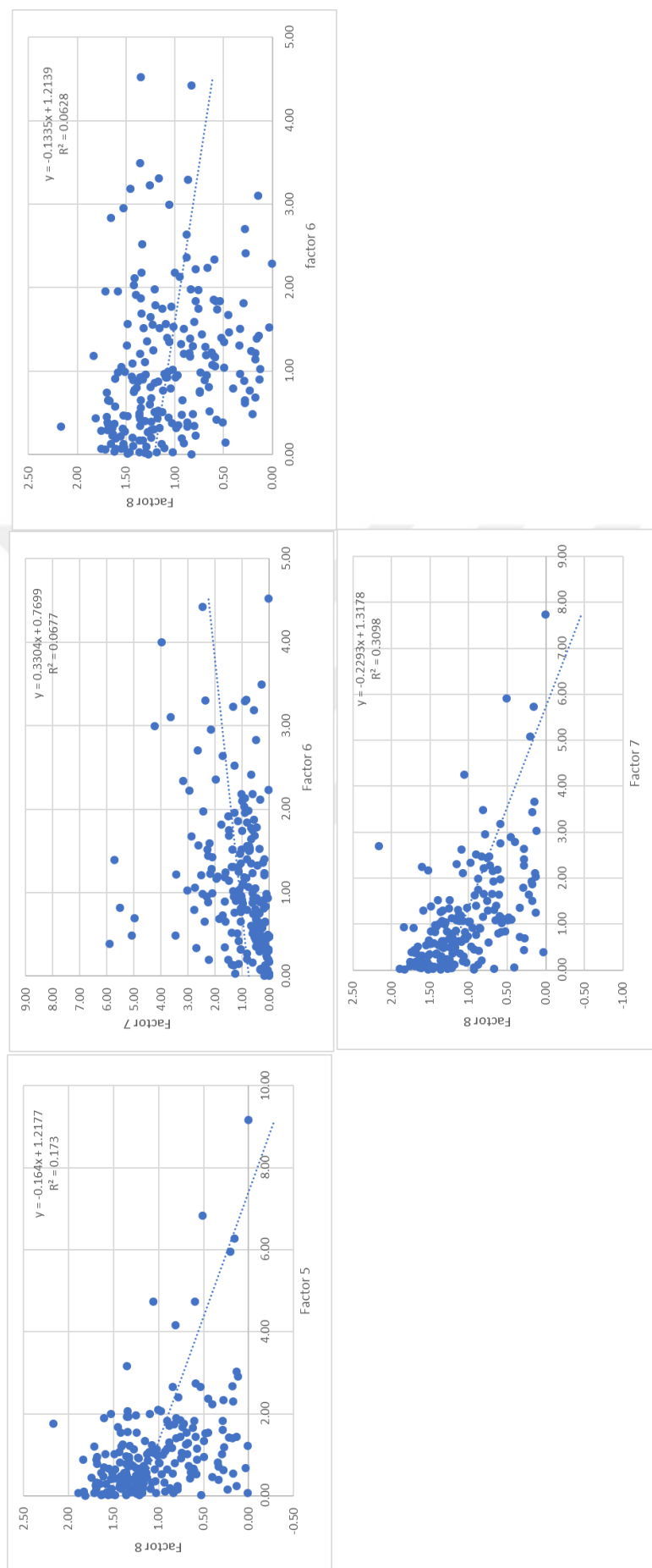


Figure 4.27. G space plots of factors for the PM_{2.5-10} analysis (continued)

Table 4.11. The relationships of predicted concentrations by PMF and observed median concentrations of parameters (ng.m⁻³)

	Predicted	Observed	Predicted /Observed		Predicted	Observed	Predicted/ Observed
Li	0.23	0.20	1.13	Ba	6.52	6.25	1.04
Na	256	261	0.983	La	0.208	0.135	1.54
Mg	256	256	1.00	Ce	0.463	0.274	1.69
Al	819	811	1.01	Pr	0.0389	0.0281	1.38
K	80.2	75.9	1.06	Nd	0.112	0.0925	1.21
Ca	860	827	1.04	Sm	0.0187	0.0159	1.18
Sc	0.45	0.54	0.843	Eu	0.00491	0.00485	1.01
Ti	20.1	18.0	1.12	Gd	0.0223	0.0191	1.17
V	0.657	0.631	1.04	Dy	0.0159	0.0135	1.17
Cr	23.3	27.2	0.855	Er	0.00909	0.00823	1.10
Mn	5.47	5.09	1.07	Yb	0.00830	0.00683	1.22
Fe	308	300	1.03	Hf	0.0187	0.0177	1.06
Co	0.252	0.219	1.15	W	0.0562	0.0653	0.860
Ni	4.08	2.88	1.42	Hg	0.0187	0.0201	0.932
Cu	2.44	2.19	1.12	Tl	0.00747	0.00710	1.05
Zn	7.96	7.25	1.10	Pb	1.04	1.12	0.926
As	0.189	0.194	0.974	Bi	0.0116	0.0131	0.884
Rb	0.341	0.292	1.17	Th	0.0365	0.0309	1.18
Sr	2.14	1.87	1.15	U	0.0154	0.0142	1.09
Y	0.0863	0.0706	1.22	Cl-*	1185	1370	0.865
Mo	0.175	0.192	0.910	NO₃⁻*	762	678	1.12
Cd	0.0327	0.0277	1.18	SO₄²⁻	600	777	0.772
Sb	0.229	0.217	1.05	NH₄⁺	38.5	362	0.106
Cs	0.0314	0.0259	1.21				

Cerium and La are the tracer elements of the automobile gasoline (Calvo et al., 2013). Copper, Mo, Fe, Cd, Mn, and Cr are emitted to the atmosphere from brake and tyre wear (EC, 2004). In addition, car brake dust contains Fe, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Sb (Hildemann et al., 1991; Legret and Pagotto, 1999; Garg et al., 2000; Kennedy et al., 2002; Westerlund and Johansson, 2002; Kennedy and Gadd, 2003). In the first factor, La, Ce, Pr and Cd were highly seen. Cobalt, Ni, Cu, Cr, Mn, Mo, Sb, W, Hg, Pb, were also observed. Whereas La, Ce, Pr and Cd were found 40% in the factor, the explained part of concentrations of elements Co, Ni, Cu, Cr, Mn, Mo, Sb, W, Hg, and Pb were below 20%. This factor indicated traffic factor. G scores were greater in May, June, May and July -2013. December- 2013 had the lowest G scores and showed a little difference between each other. The daily variations of G scores were shown in Figure 4. 28. The highest G score was observed in 09/06/2013. In this factor, Sb, Cd, Hg, Cr, Mo, Ni were highly enriched. Lead, Cu, W, Ce, La, Co, Ba were moderately enriched (Figure 4.29). East (TEM and D-100 highways), SE (city center), S directions were the dominant wind sectors. The campus traffic effect was seen from the WSW and SW directions. Figure 4.30 shows the graph of Factor 1.

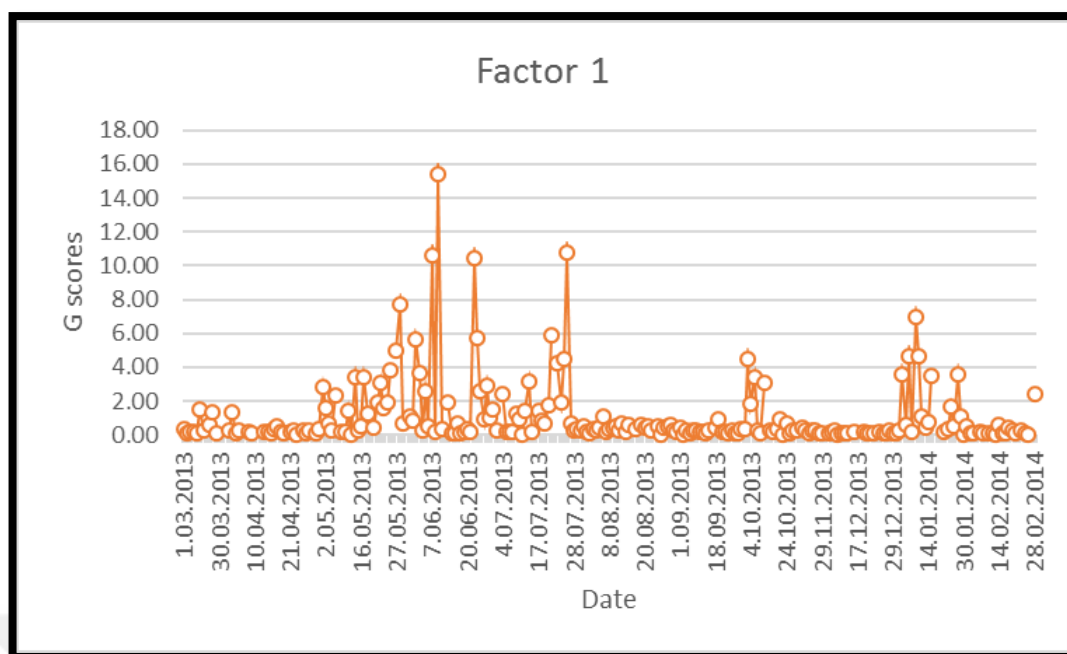


Figure 4.28. Daily variations of G-scores for Factor 1 in PM_{2.5-10}

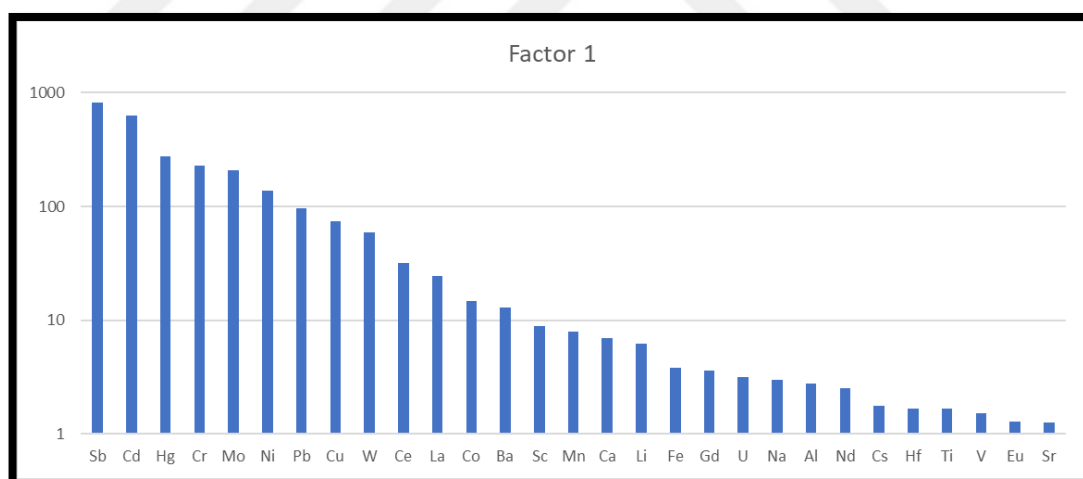


Figure 4.29. The enrichment factor values in Factor 1 for PM_{2.5-10}

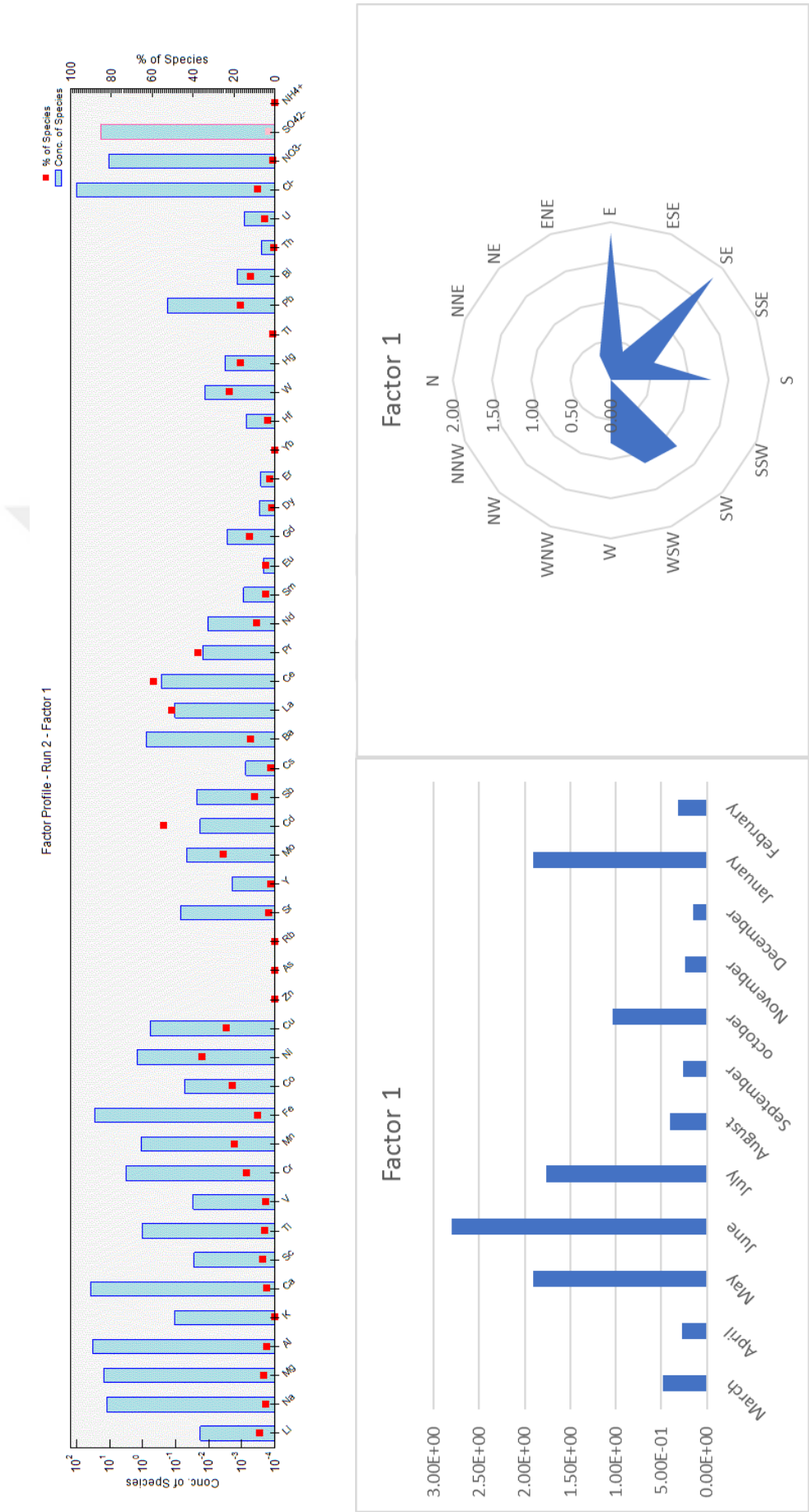


Figure 4.30. PMF results of Factor 1 for PM_{2.5-10}

Coal contains As, Cd, Hg, Mo, Pb, Sb, Tl, V, Ni, Zn. As, Cd, Hg, and Mo are the most hazardous elements found in coal (Finkelman and Gross, 1999). Peoples around the sampling points were heating by using coal and biomass burning and As is a tracer elements in Turkish lignites (Yenisoy Karakaş, 2000). In the second factor, Tl, Bi, As, were highly explained. Cadmium, Sb, Pb, W, Hg, Cs were also observed in Factor 2. Whereas Tl was explained in greatest percentage (60%), explained part of As and Bi were in 40% in the factor. Antimony, Cd, Pb, W, Hg, Bi were observed nearly 20%. Therefore, this factor points out that coal burning should be affecting the sampling point. The highest G scores were observed in March and G scores decreases with summer months. The daily variations of G scores were shown in Figure 4.31. In this factor, Sb, As, Cd, Pb, Mo, Hg, Cr, Zn, W were highly enriched, Ni, Cs, Sc, Cu, Al, Fe, V, U and Rb were moderately enriched and the rest of the analyzed elements by PMF analysis were nonenriched (Figure 4.32). G score was also used to illustrate pollution roses for the factor. The highest G scores were observed from the air masses through ESE sector (Figure 4.33). This figure was also compared with the pollution roses of As, Bi and Tl. These comparisons also supported our explanation. Because air masses came the sampling area from ESE sector which indicates the residential areas.

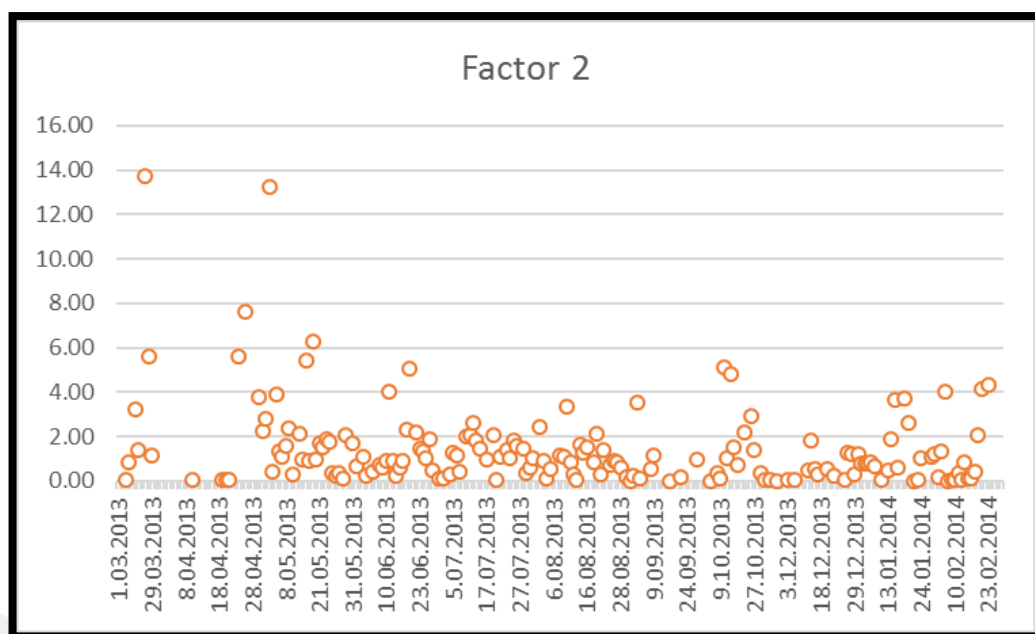


Figure 4.31. Daily variations of G-scores for Factor 2 in PM_{2.5-10}

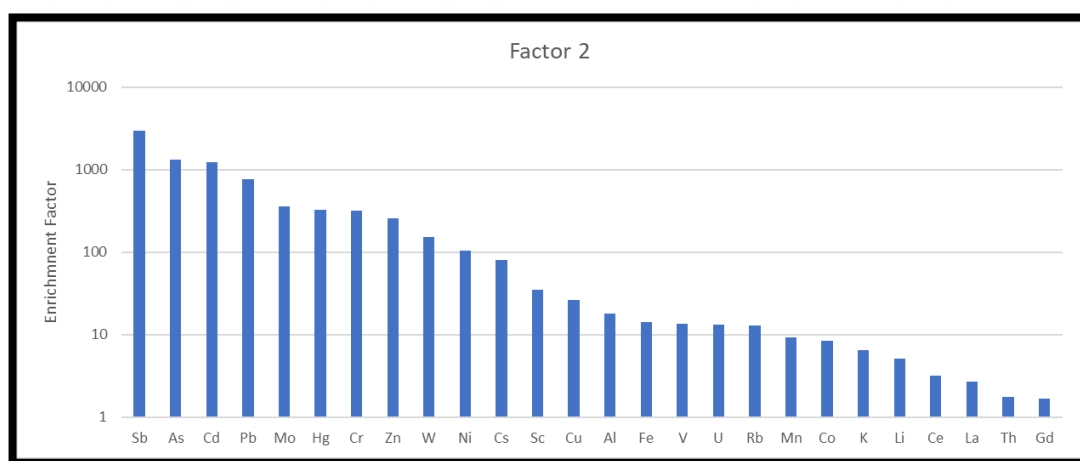


Figure 4.32. The enrichment factor values in Factor 2 for PM_{2.5-10}

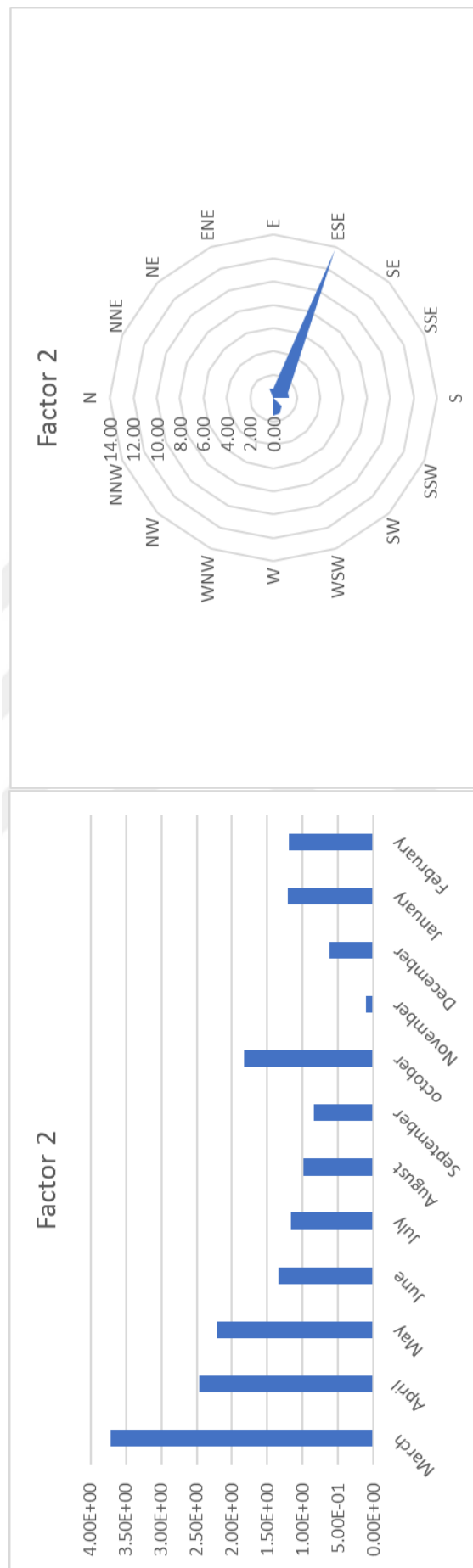
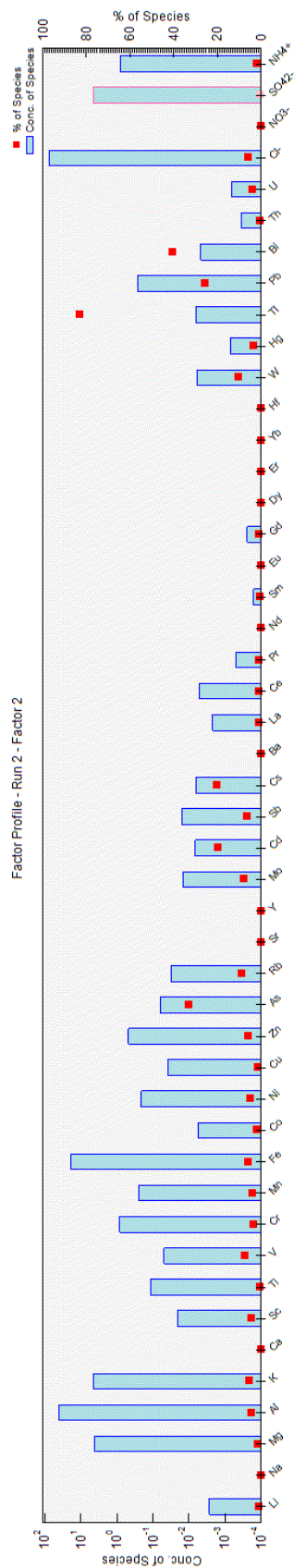


Figure 4.33. PMF results of Factor 2 for PM_{2.5-10}

In Factor 3, NO_3^- , SO_4^{2-} were highly observed. Barium, Fe, Hg, Pb, As, NH_4^+ , Cl^- , were also seen. Sulfate and NO_3^- were explained higher than 80%. Because of the dominance of secondary inorganic aerosols, this factor is called aged particles. Figure 4.34 shows the HYSPLIT trajectory model of the date. G scores were greater in April, in July, and in August 2013. May had the lowest G scores. The highest G score was observed in 19/01/2014 (Figure 4.35). In this factor, Sb, Cr, Hg, Cd, As, Pb, Zn, Ba and Sc are highly enriched elements (Figure 4.36). South-West, East and South-East sectors were the dominant wind sectors. Figure 4.37 shows the graph of Factor 3.

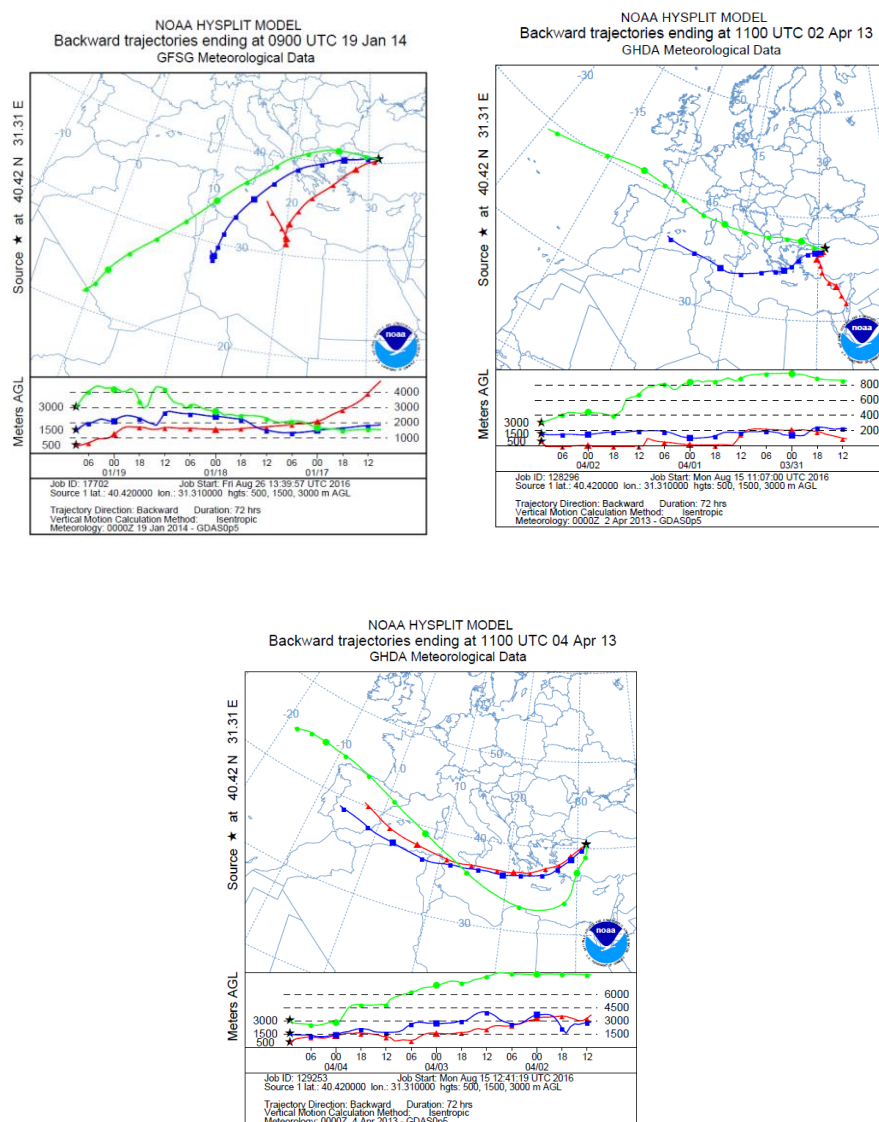


Figure 4.34. Back trajectory of date which has the highest G score for Factor 3 in $\text{PM}_{2.5-10}$

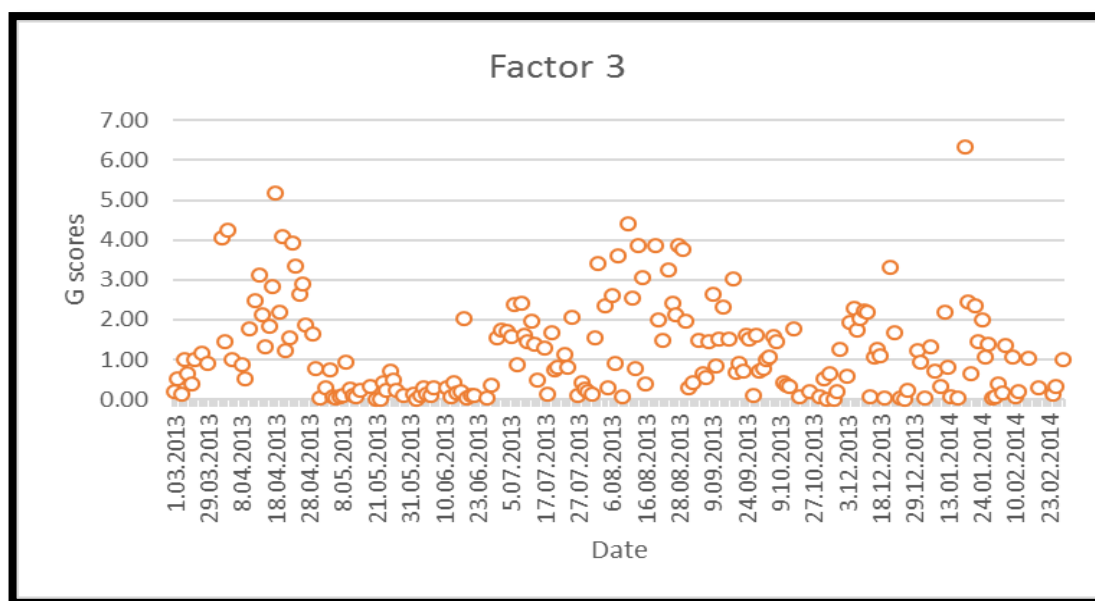


Figure 4.35. Daily variations of G scores for Factor 3 in PM_{2.5-10}

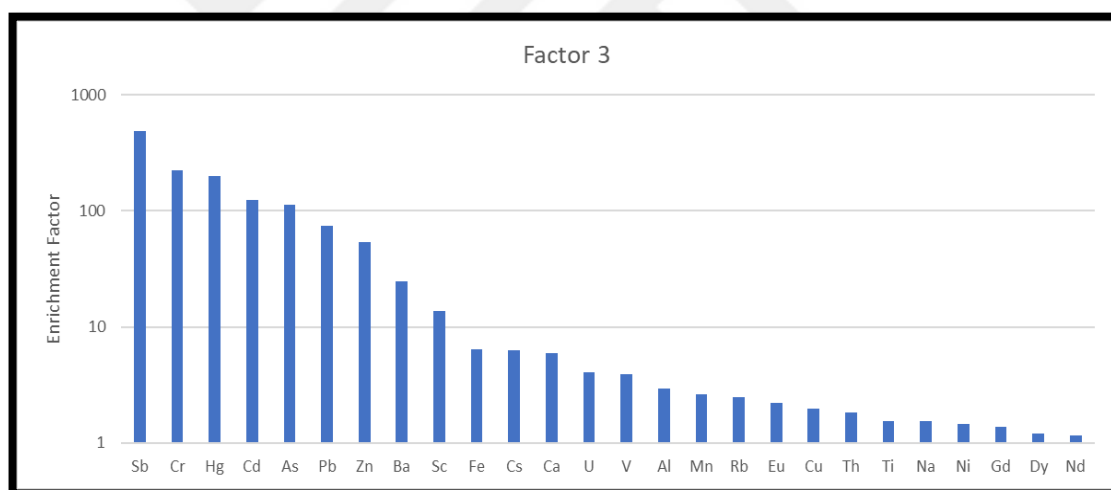


Figure 4.36. The enrichment factor values in Factor 3 for PM_{2.5-10}

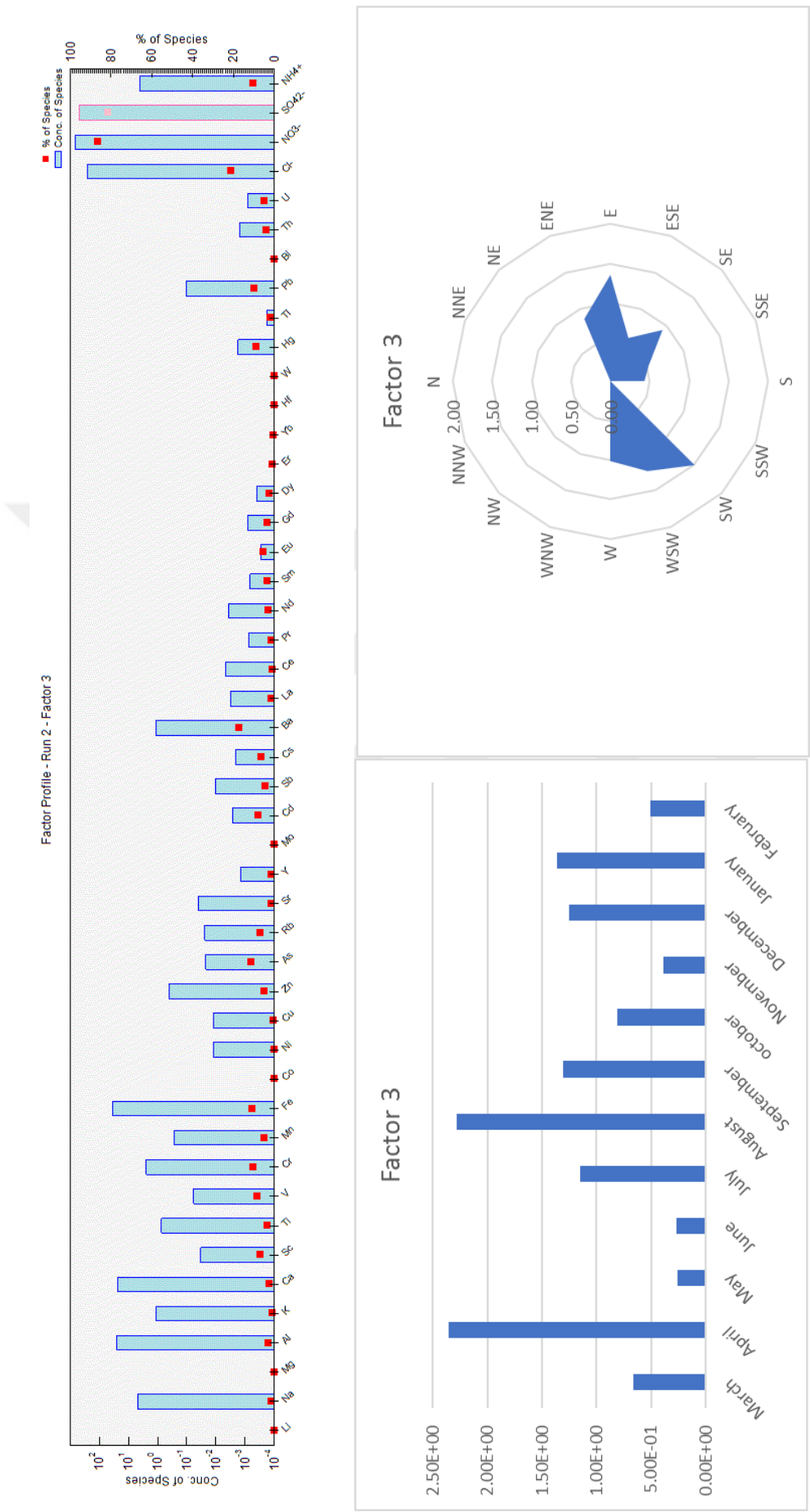


Figure 4.37. PMF results of Factor 3 for PM_{2.5-10}

Figure 4.38 illustrates the results of Factor 4. In this factor, NH_4^+ and K were observed in a great percentage (higher than 40%). Lead, Bi, Sb, Mo, Cu, Zn, Na, Mg, and Hf were also explained in the factor. There are some agricultural areas and fertilizer contains NH_4^+ which is used around the sampling area. Monthly variations were evaluated. Between May and October, farmers burn fields after harvest. Therefore, this property indicated biomass burning. G scores were greater in May 2013. December 2013 had the lowest G scores (Figure 4.39). Generally, highest G score were observed the air masses came from ESE, W and WSW sectors. There are villages in these sectors and they used wood for heating. They also burn their wastes. Potassium and Sb is the tracer of garbage burning (Christian et al., 2010). Antimony, Zn, Mo, Pb, Cu were highly enriched elements whereas Na, W, K, Hf, Li, Ba, Cd, Rb, Cs, Eu were moderately enriched elements in Factor 4 (Figure 4.40).

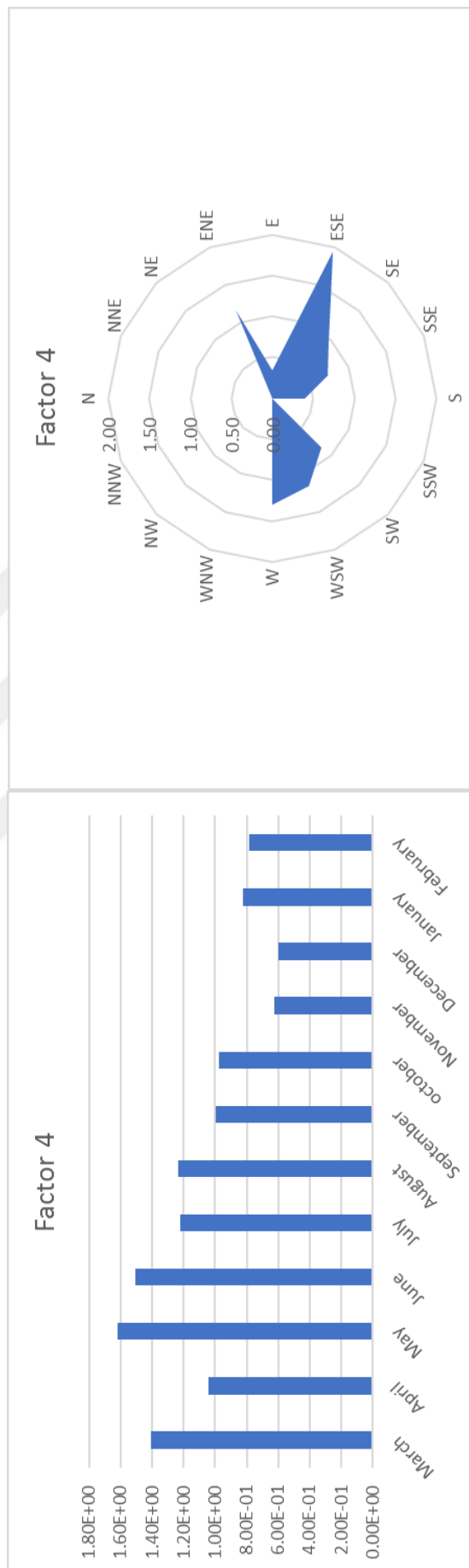
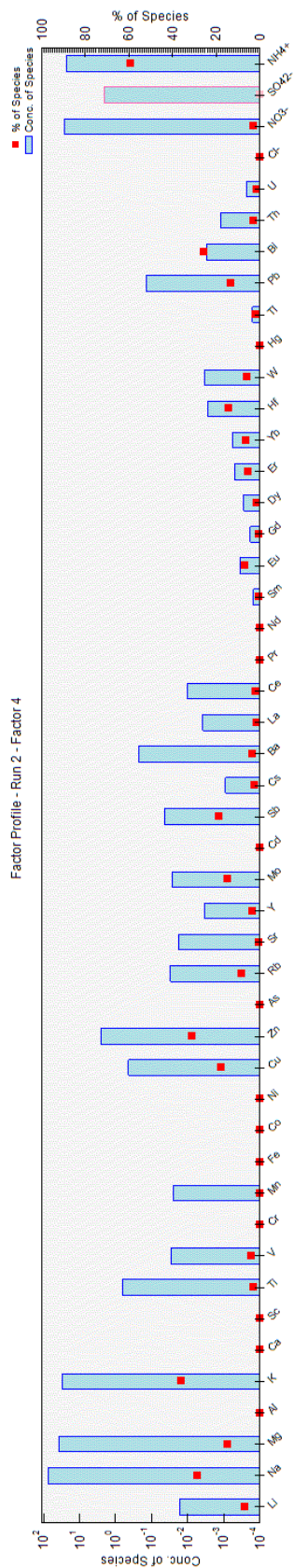


Figure 4.38. PMF results of Factor 4 results for PM_{2.5-10}

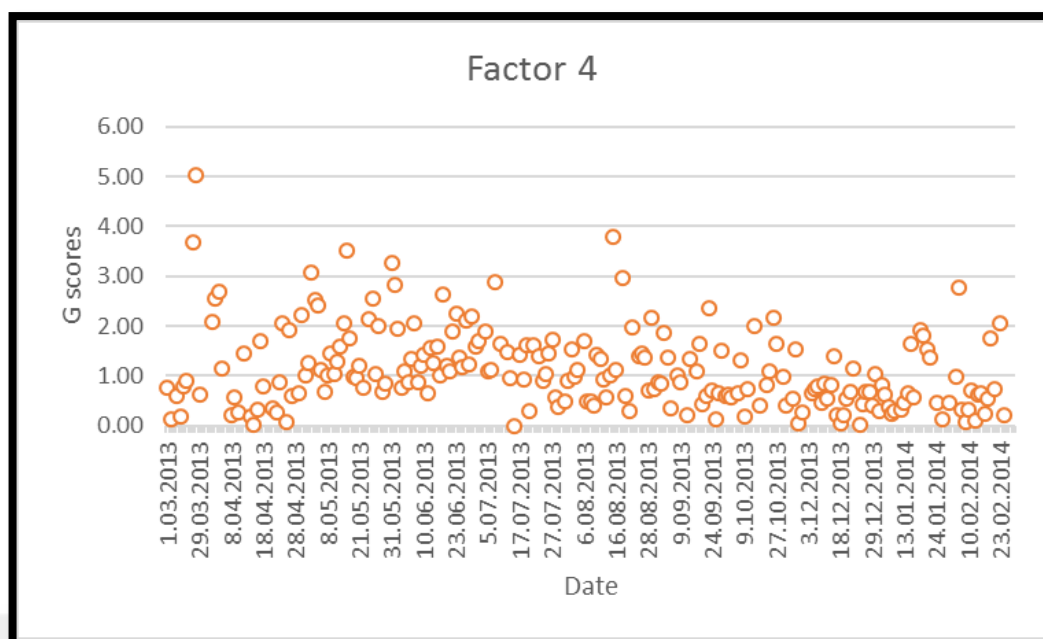


Figure 4.39. Daily variations of G scores for Factor 4

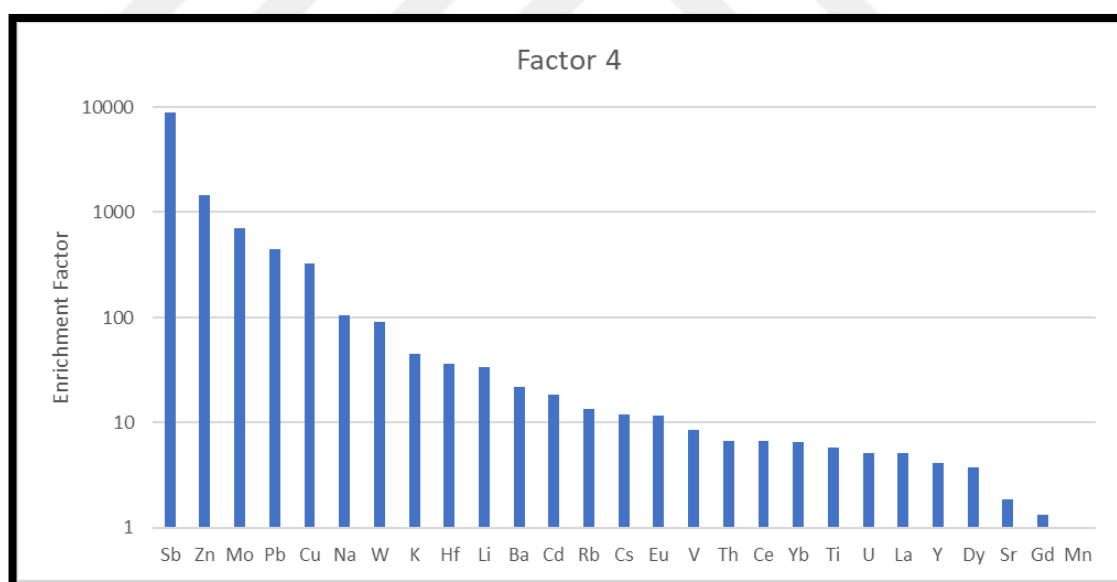


Figure 4.40. The enrichment factor values in Factor 4 for $PM_{2.5-10}$

Figure 4.41 illustrates the results of factor 5. In this factor, soil elements like Sr, Y, Rb, Pr, Nd, Sm, Dy, Er, Ti, La, Ce, Eu, Gd, Yb, Hf, Th, U were highly observed. Anthropogenic elements like As and Cr, were also seen in the factor. Strontium, Y, Rb, Pr, Nd, Sm, Dy, Er, Hf, Th, Co, Fe, Mn, V, Ca, Li were observed higher than 40%. This indicated soil factor. G scores increased in March and in May 2013 because of the high suspended soil dust coming from planting activities. The lowest G scores were observed in December 2013 (Figure 4.42). 23/05/2013 has the greatest G scores. There are agricultural activities in S direction. Pollution roses of Sr Y, Rb, Pr, Nd, Sm, Dy, Er, Ti, La, Ce, Eu, Gd, Yb, Hf, Th, U and wind sector analysis of G scores were also compared and the interpretation supported the polluted soil factor. In this factor, there were not any highly or moderately enriched elements (Figure 4.43)



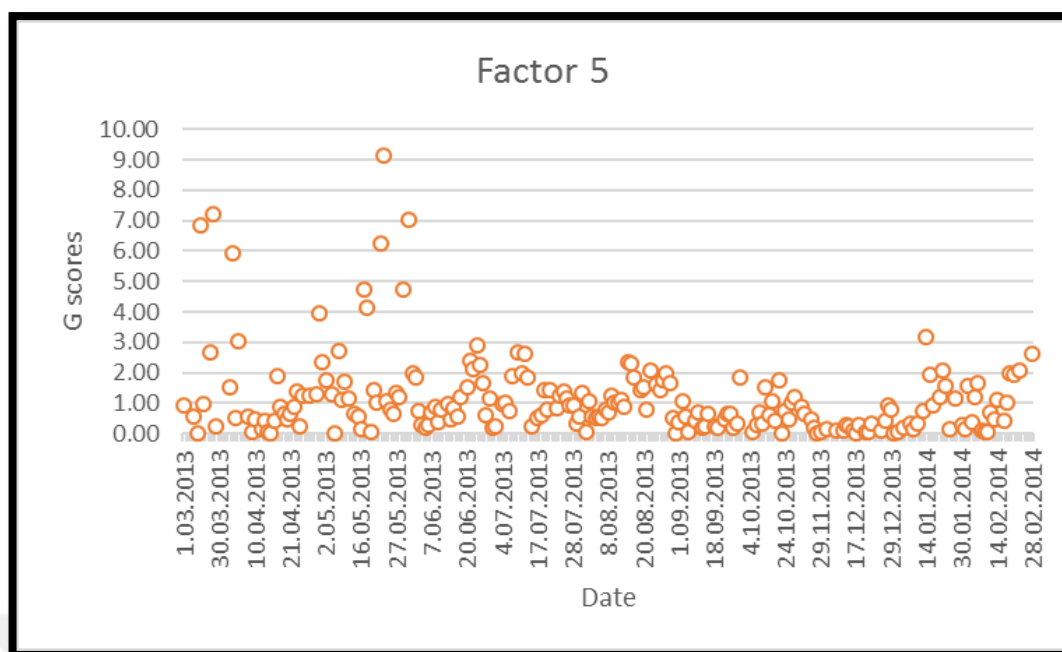


Figure 4.42. Daily variations of G-scores for Factor 5 in PM_{2.5-10}

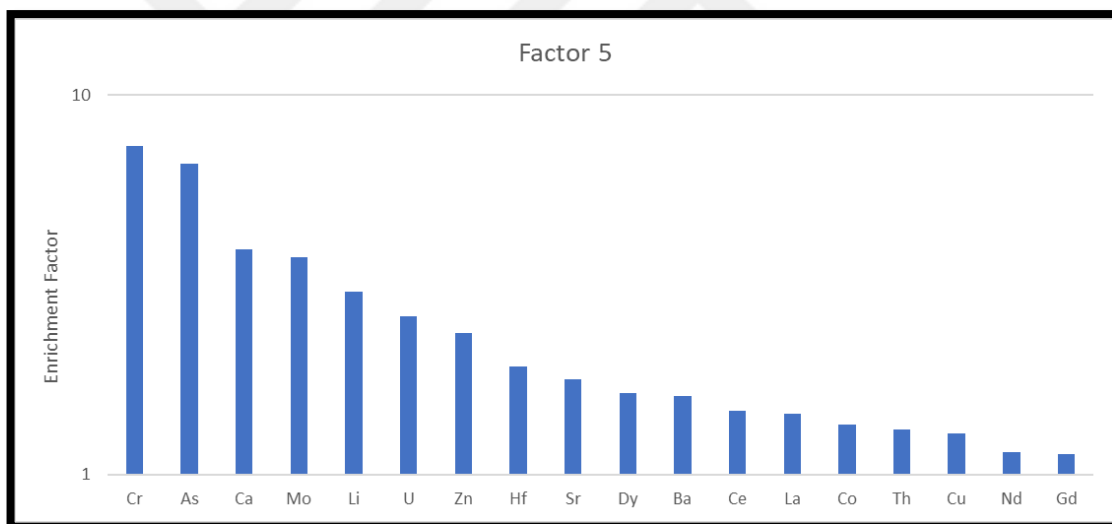


Figure 4.43. The enrichment factor values in Factor 5 for PM_{2.5-10}

Lithium, Ca, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Sb, Ba, Pb, were observed in Factor 6. Antimony had the highest percentage (60%). In this factor Sc was selected as a crustal element, since the concentration of Sm was given as zero in the output of the program. Antimony was the highest enriched element in the factor 6 (Figure 4.44). Copper, Fe, Ni, Zn were explained higher than 20%. It indicated that iron, steel industry. The highest G score observed in May whereas the lowest G scores were obtained in December (Figure 4.45). The winds coming from South East, East North-

East and West sectors were dominant in the factor (Figure 4.46). The highest G score was determined in 14/01/2014 (Figure 4.47).

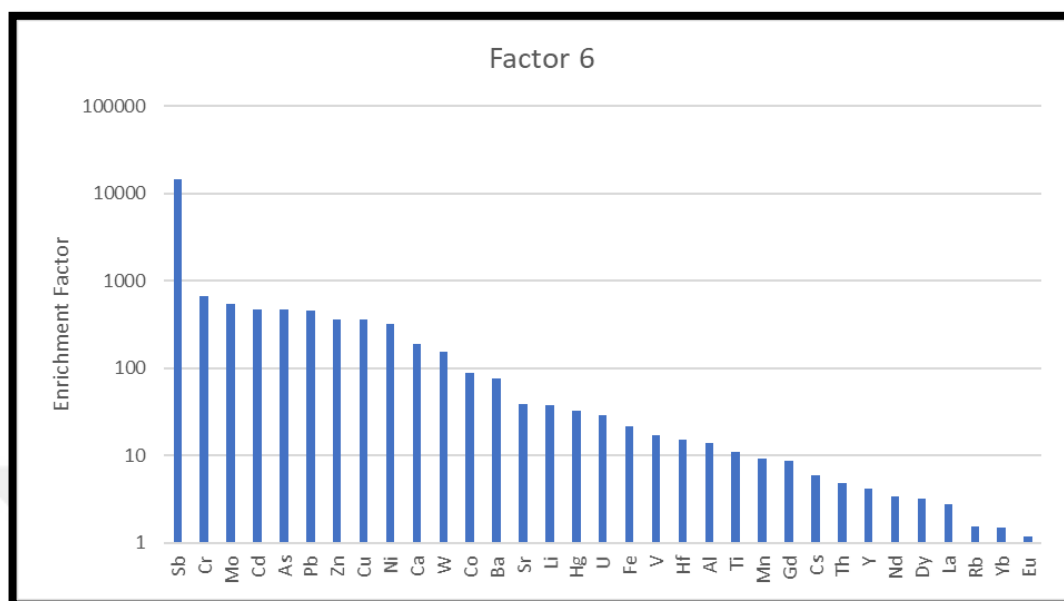


Figure 4.44. The enrichment factor values in Factor 6 for PM_{2.5-10}

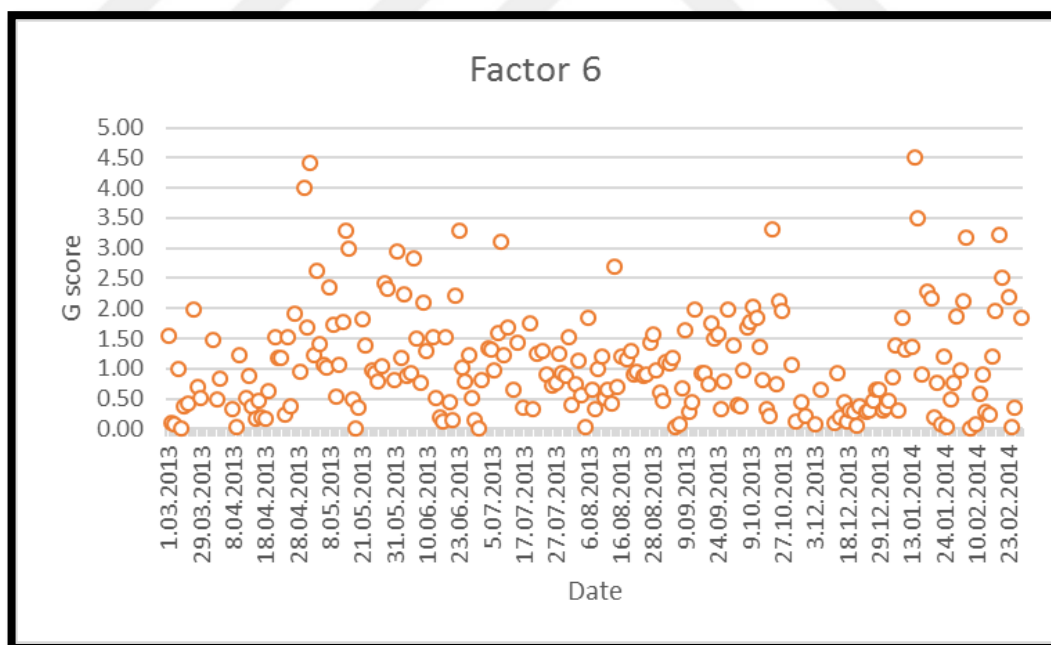


Figure 4.45. Daily variations of G-scores for Factor 6 in PM_{2.5-10}

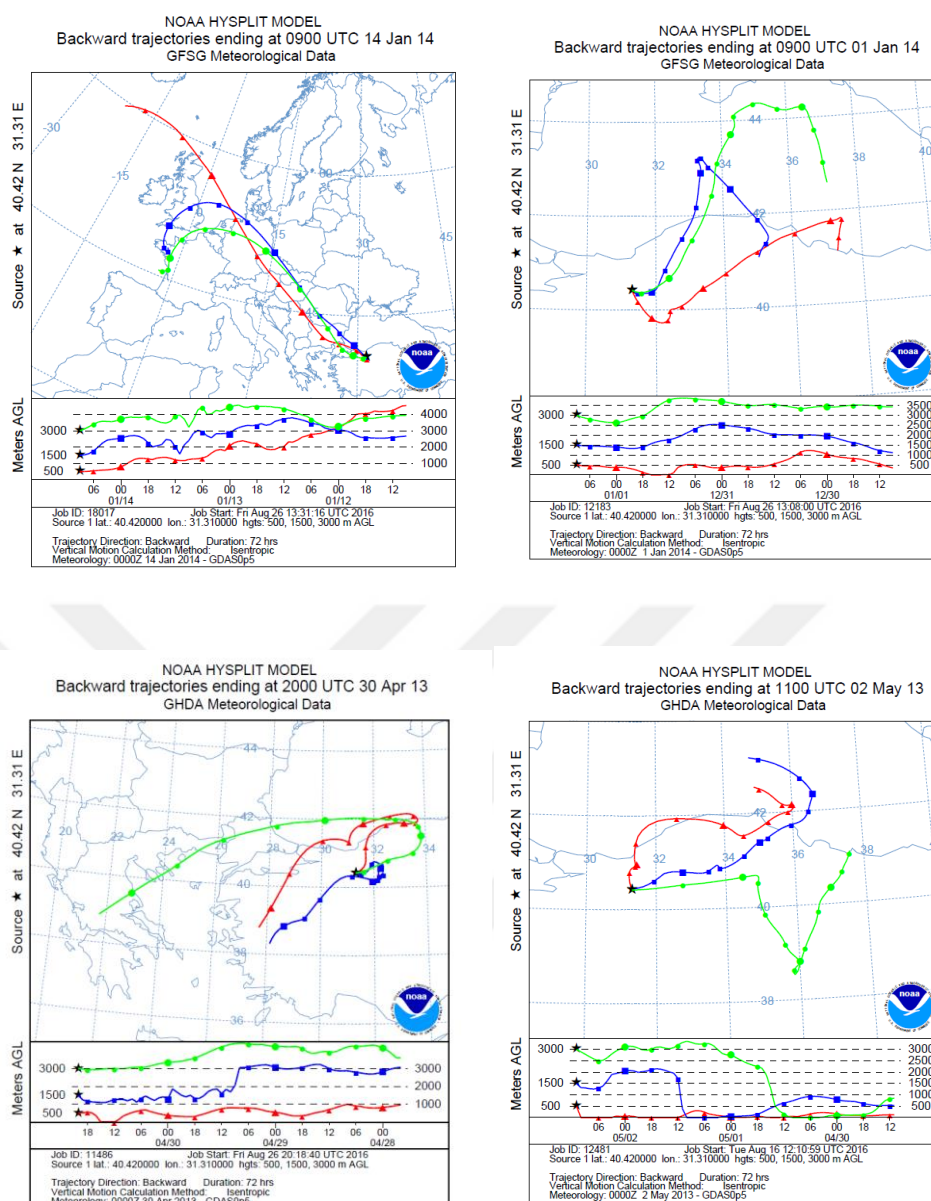


Figure 4.47. Back trajectory of date which has the high G score

Figure 4.48 illustrates the results of factor 7. In this factor, soil elements like Li, Mg, Al, K, Ca, Sc, V, Mn, Fe, Y, Rb, Pr, Nd, Sm, Dy, Er, Ti, La, Ce, Eu, Gd, Yb, Hf, W, Th, U were observed. In addition, G scores of spring and summer months were higher than winter months. The lowest G scores were observed in December 2013 (Figure 4.49). The wind sector analysis of G scores was also similar with the pollution roses of soil elements like Ti, Nd and Sm. In addition, there were no highly enriched elements in the factor 7. Mercury and Sb were moderately enriched in the factor (Figure 4.50). The air came from S sector affected the factor. This indicated soil factor.

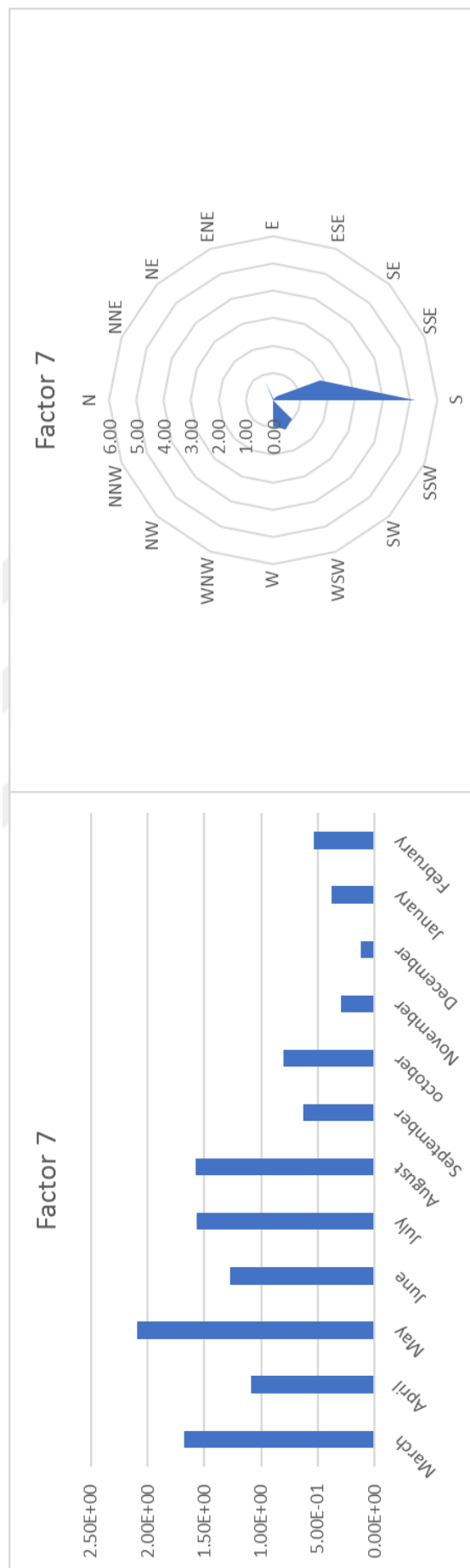
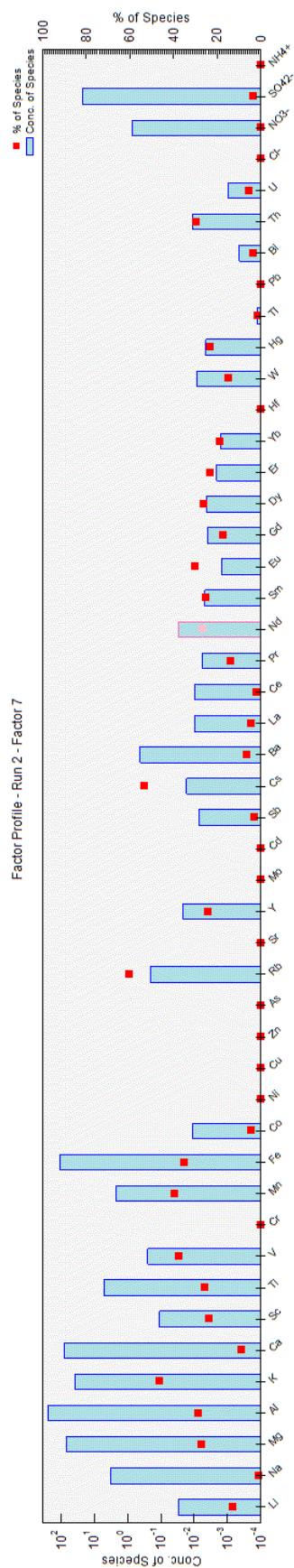


Figure 4.48. PMF results of Factor 7 for $PM_{2.5-10}$

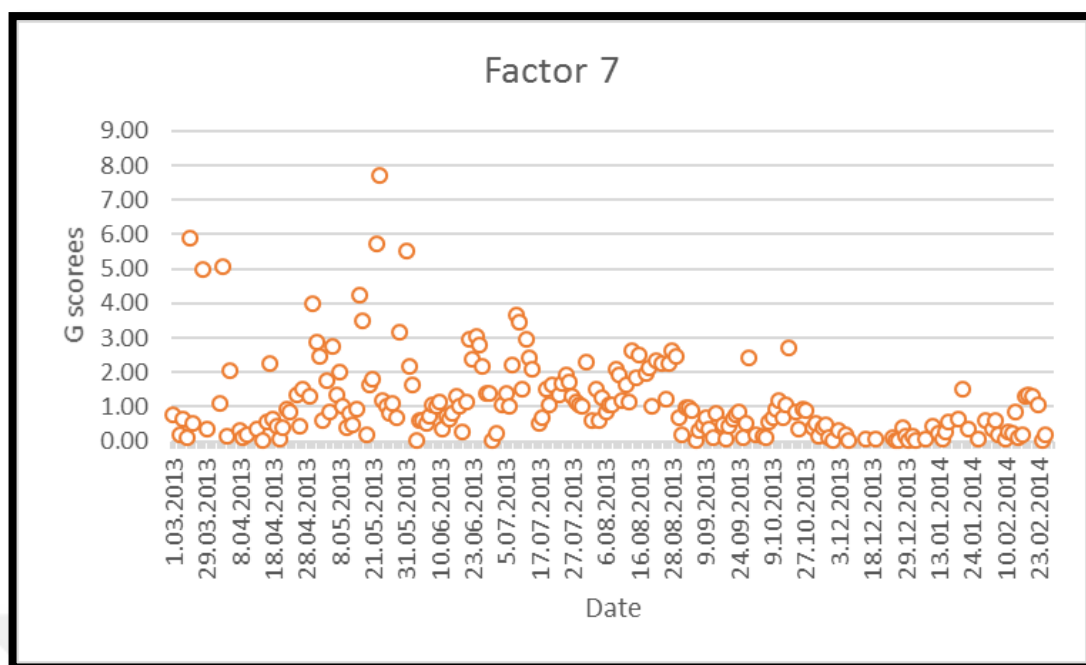


Figure 4.49. Daily variations of G-scores for Factor 7 in PM_{2.5-10}

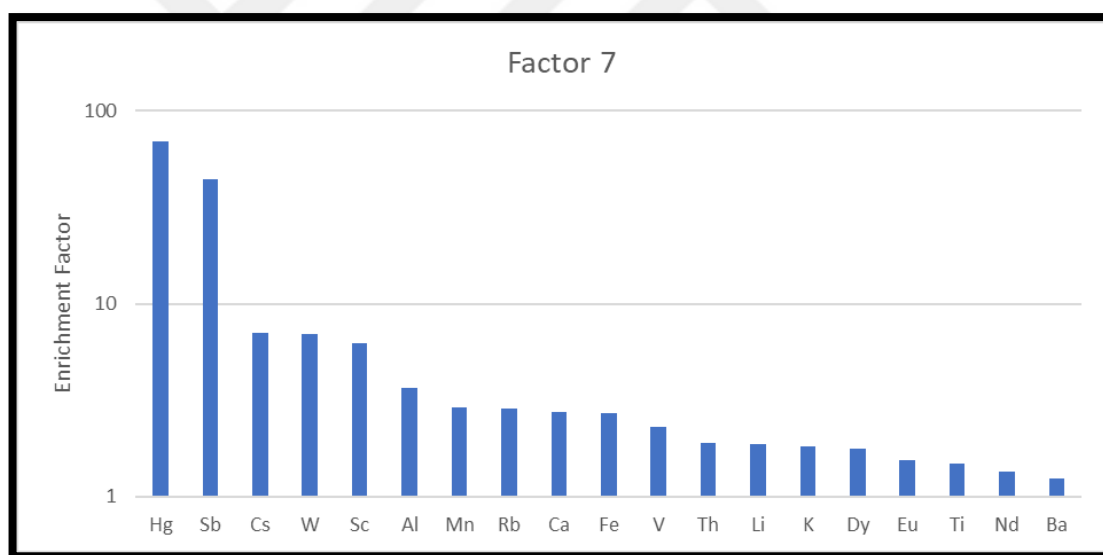


Figure 4.50. The enrichment factor values in Factor 7 for PM_{2.5-10}

Ammonium, Cl^- , Na, Mg, Al, Ca, Sc, Fe, Cr were explained in the last factor. Antropogenic elements like Co, Ni, Cu, Zn, As were also observed (nearly 40%). This indicated the sea and long-range transportation from Russia and Europe (Figure 4. 51). Chromium, Hg, Zn, Mo were highly enriched whereas As, Ni, Sc, W, Cu, Pb, Al, Ca, Na, Ba were moderately enriched elements in the factor 8 (Figure 4. 52). The monthly and daily G scores signed the continuous contribution (Figure 4.53 and 4.54).

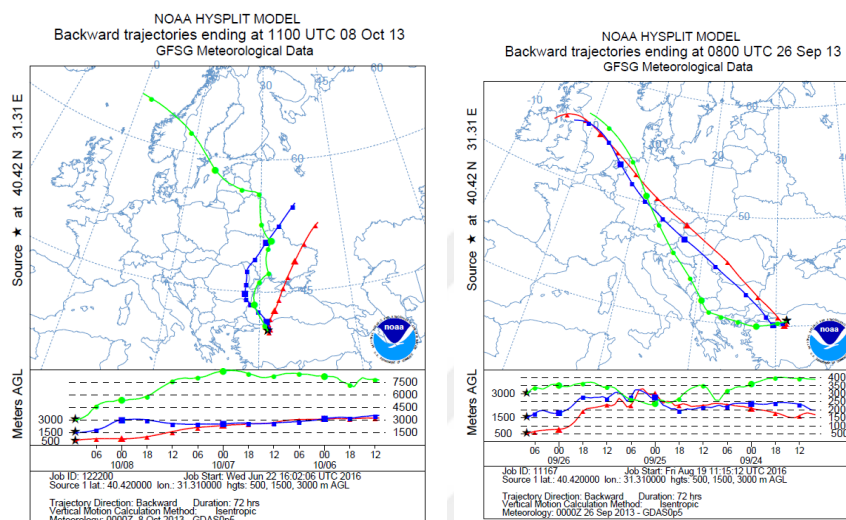


Figure 4. 51. Some examples of backtrajektroies for Factor 8 in $\text{PM}_{2.5-10}$

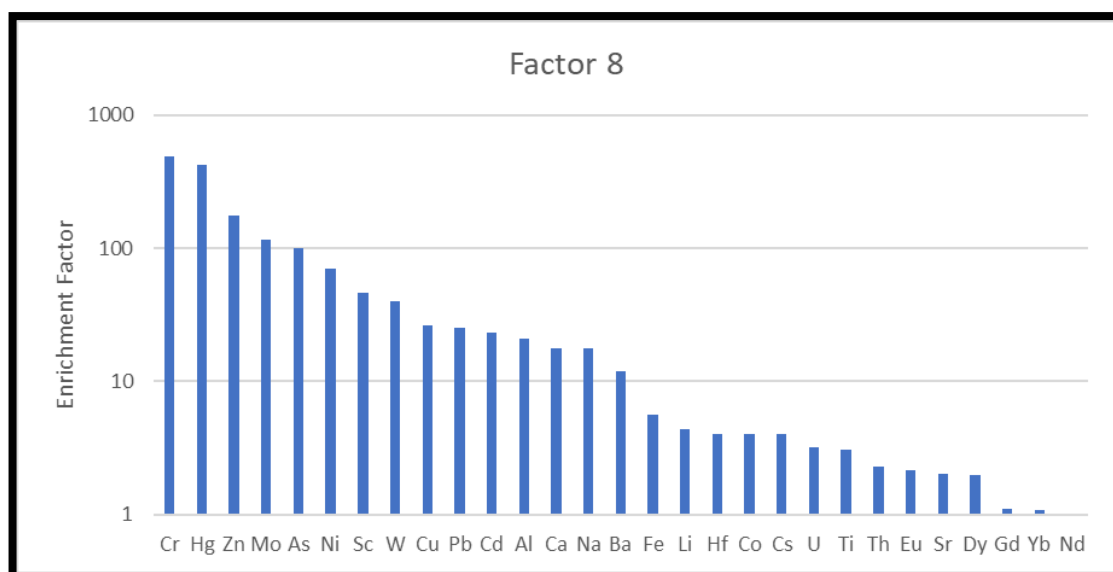


Figure 4.52. The enrichment factor values in Factor 8 for $\text{PM}_{2.5-10}$

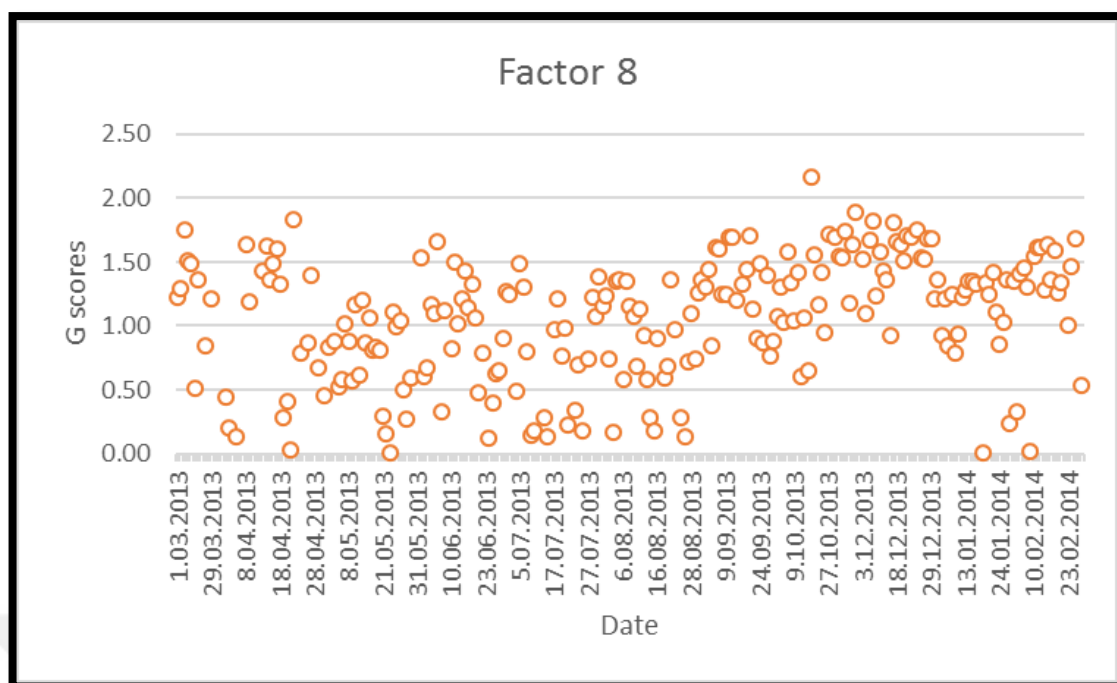


Figure 4.53. Daily variations of G-scores for Factor 8 in PM_{2.5-10}

Figure 4.55 shows the percent contribution of each factor in $PM_{2.5-10}$. The highest contribution belongs to polluted soil factor. The lowest contribution belongs to the coal burning. Aged particles and biomass burning had similar contribution to $PM_{2.5-10}$.

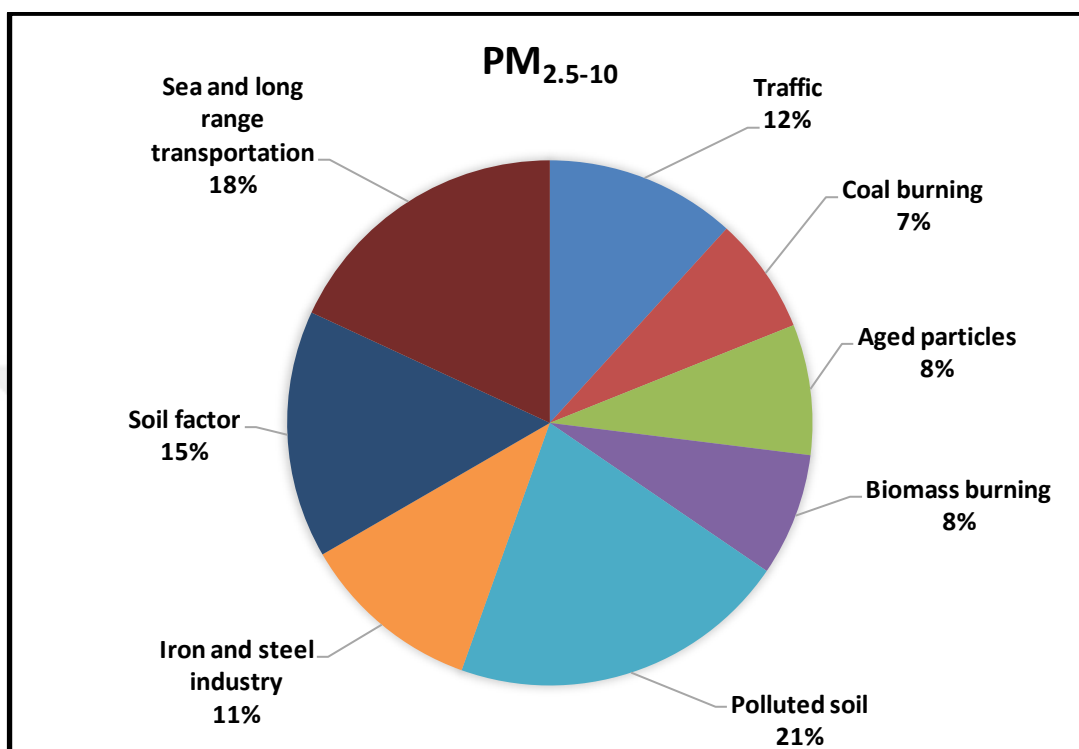


Figure 4.55. Percent contributions of each factor in $PM_{2.5-10}$

4.9.3.2 Positive Matrix Factorization results for PM_{2.5}

Base model results were evaluated as in the part 4.7.1.1. For PM_{2.5}, Ca, Sc, V, Cr, Fe, Ni, Cu, Zn, As, Mo, Cd, Ba, Eu, W, Hg, Pb, Bi, Cl⁻, NO₃⁻, SO₄²⁻, and NH₄⁺ were categorized as ‘Weak’ and Be, Sn, Se, Ge, Tb, Ho, Tm, Lu, Na⁺, K⁺, Mg²⁺, and Ca²⁺ were selected as ‘Bad’. After running base run model, Q_{theoric} value was also calculated by the equation

$$Q_{\text{theoric}} = n \cdot m - p \cdot (n+m)$$

where n is the number of species, m is the number of samples in the data set, and p is the number of factors fitted by the model (Table 4.12). G-Scores were obtained by the programme. Factor profiles showed the factor contribution in each species as a concentration and percent contribution. The combination with the daily wind sectors a graph was also obtained.

Table 4.12. The base model results of PM_{2.5}

Factor Number	Q _{theorical}	Q _{true}	Q _{robust}	Q _{robust} /Q _{theoretical}	Q _{true} /Q _{robust}
8	9776	12003.1	11679.1	1.19	1.02

The relationship between the factors was evaluated by using the correlations of factor with each other (Figure 4.56). The low r² values were found. Therefore, it was a sign for no significant relationship between the factors. The DISP error estimation studies also supported interpretation about the G space plot. The DISP result was shown below:

$$\begin{matrix} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$$

The programme did not found any error in the solution mathematically. Then, the 8 factors were evaluated and identified by using the tracer elements or ions in each factor. The predicted total concentrations by PMF for each parameter were compared

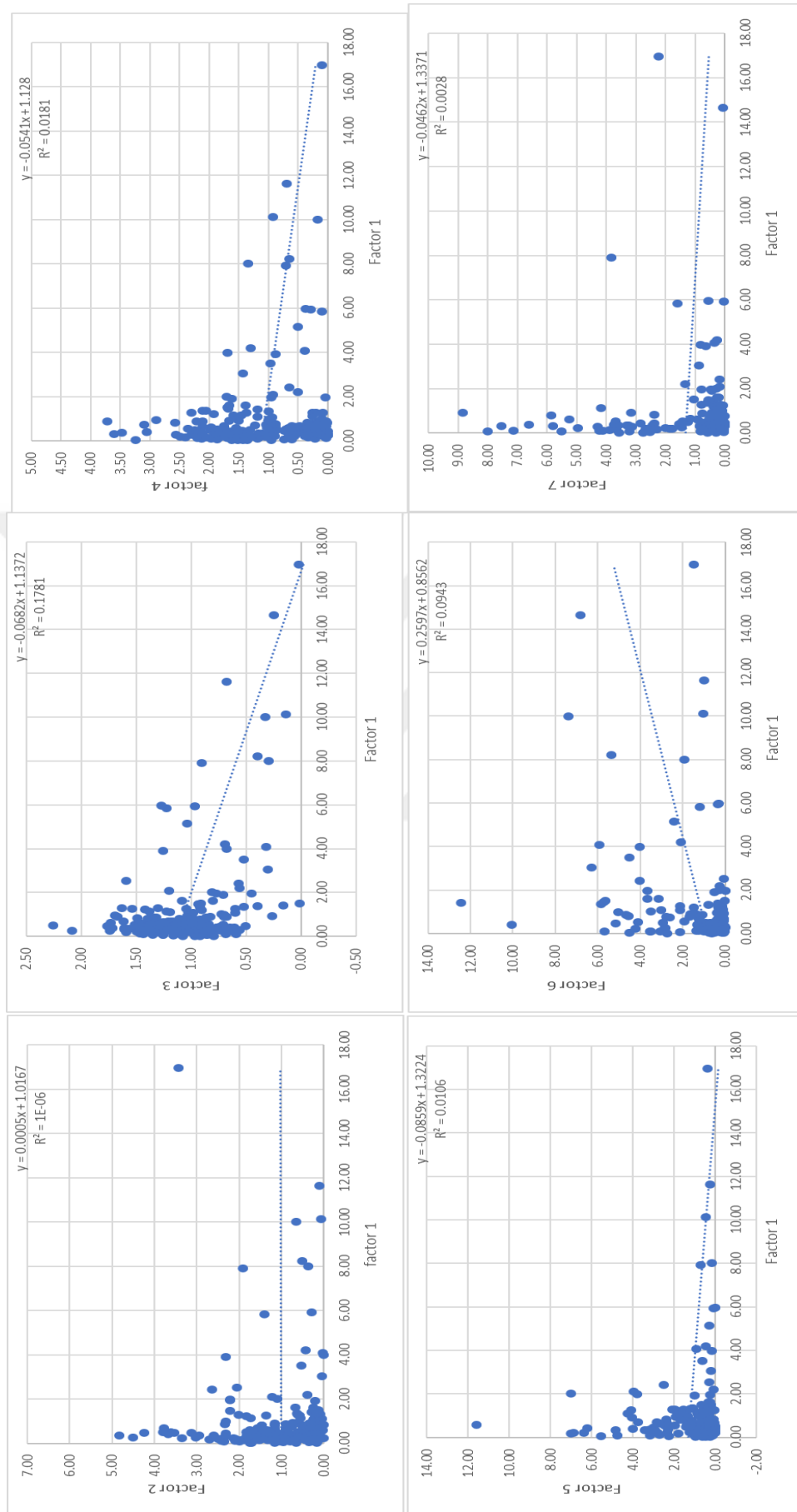


Figure 4.56. G space plots of factors for the PM_{2.5} analysis

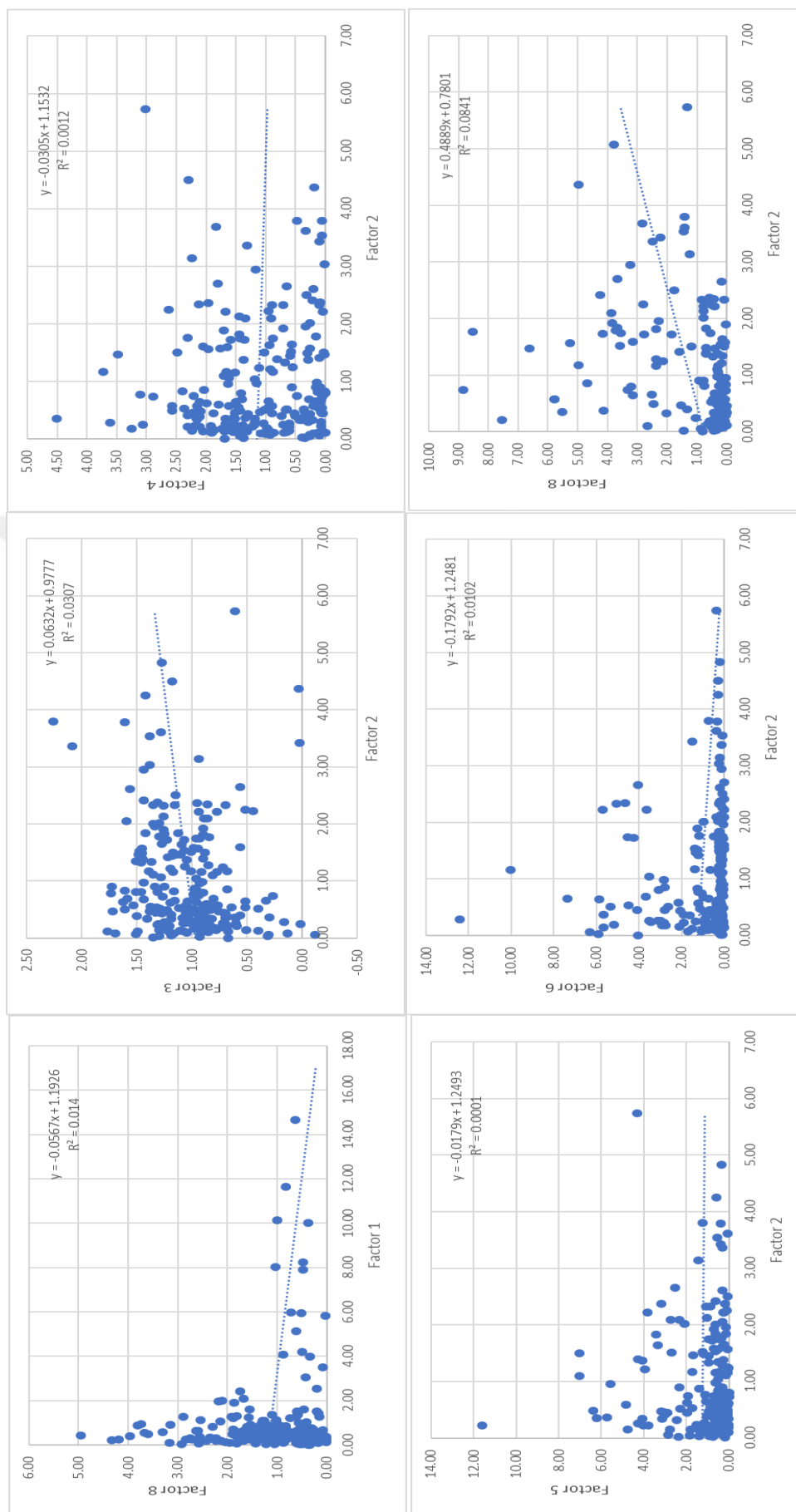


Figure 4.56. G space plots of factors for the PM_{2.5} analysis (continued)

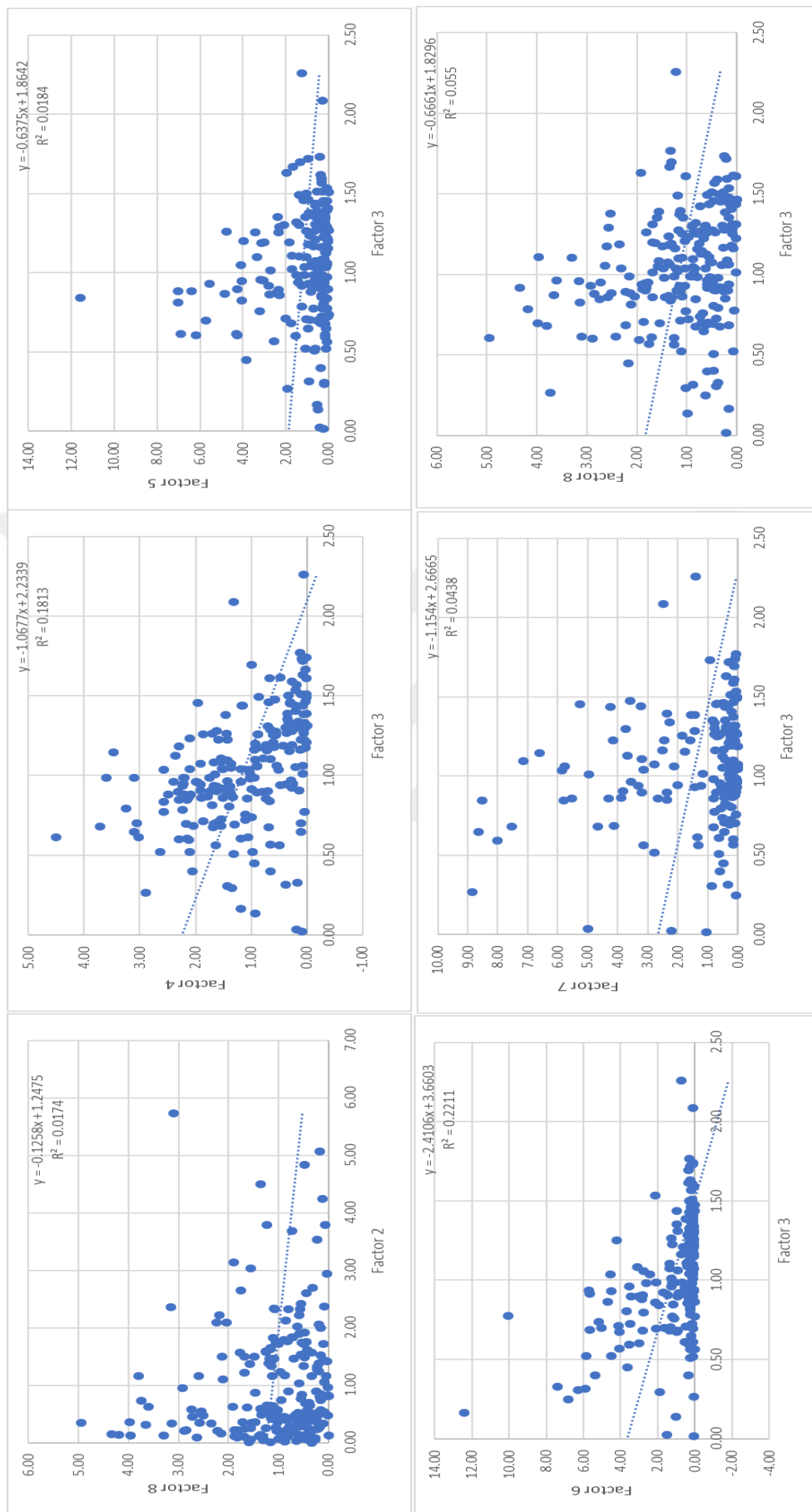


Figure 4.56. G space plots of factors for the PM_{2.5} analysis (continued)

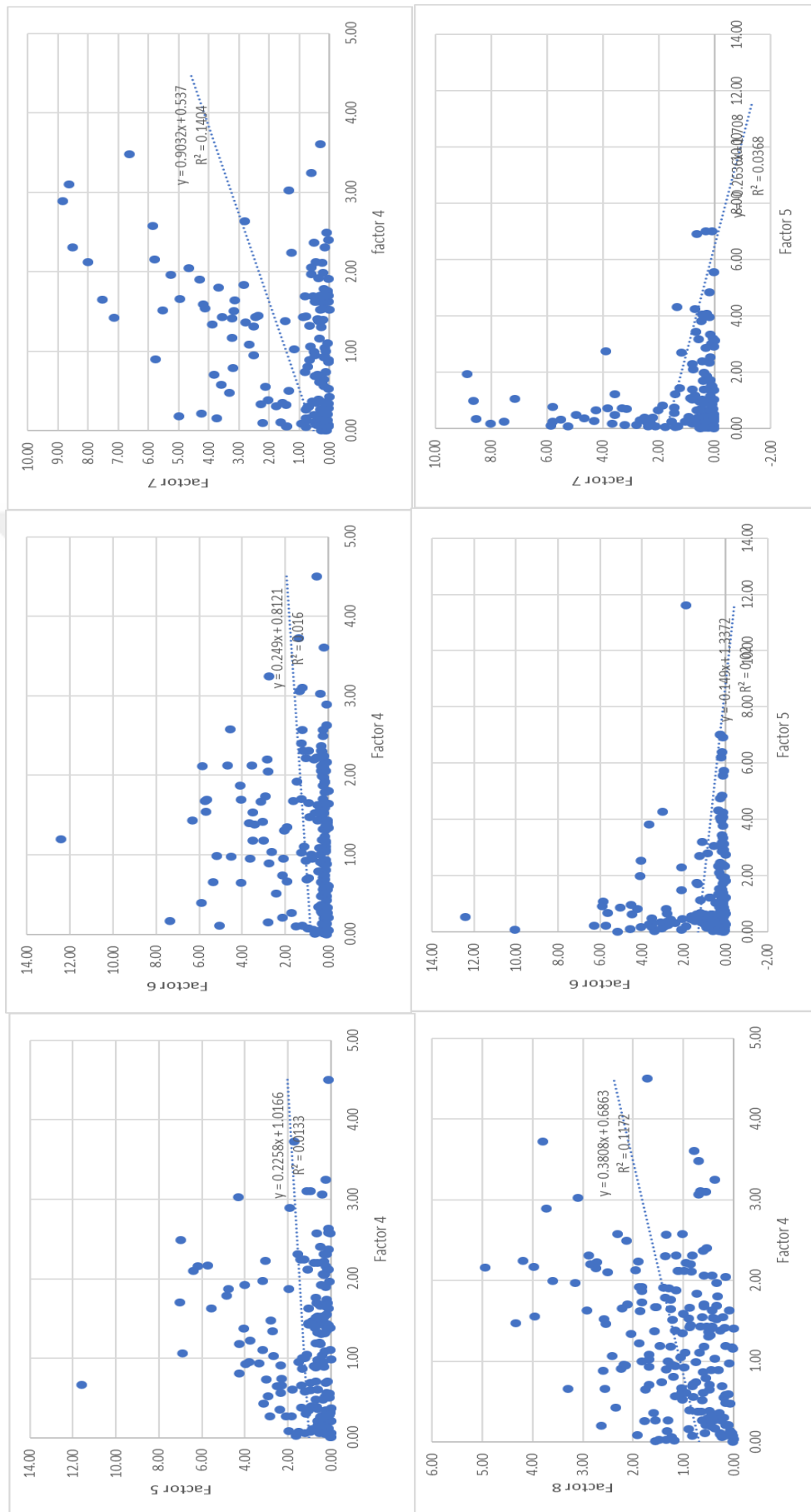


Figure 4.56. G-space plots of factors for the PM_{2.5} analysis (continued)

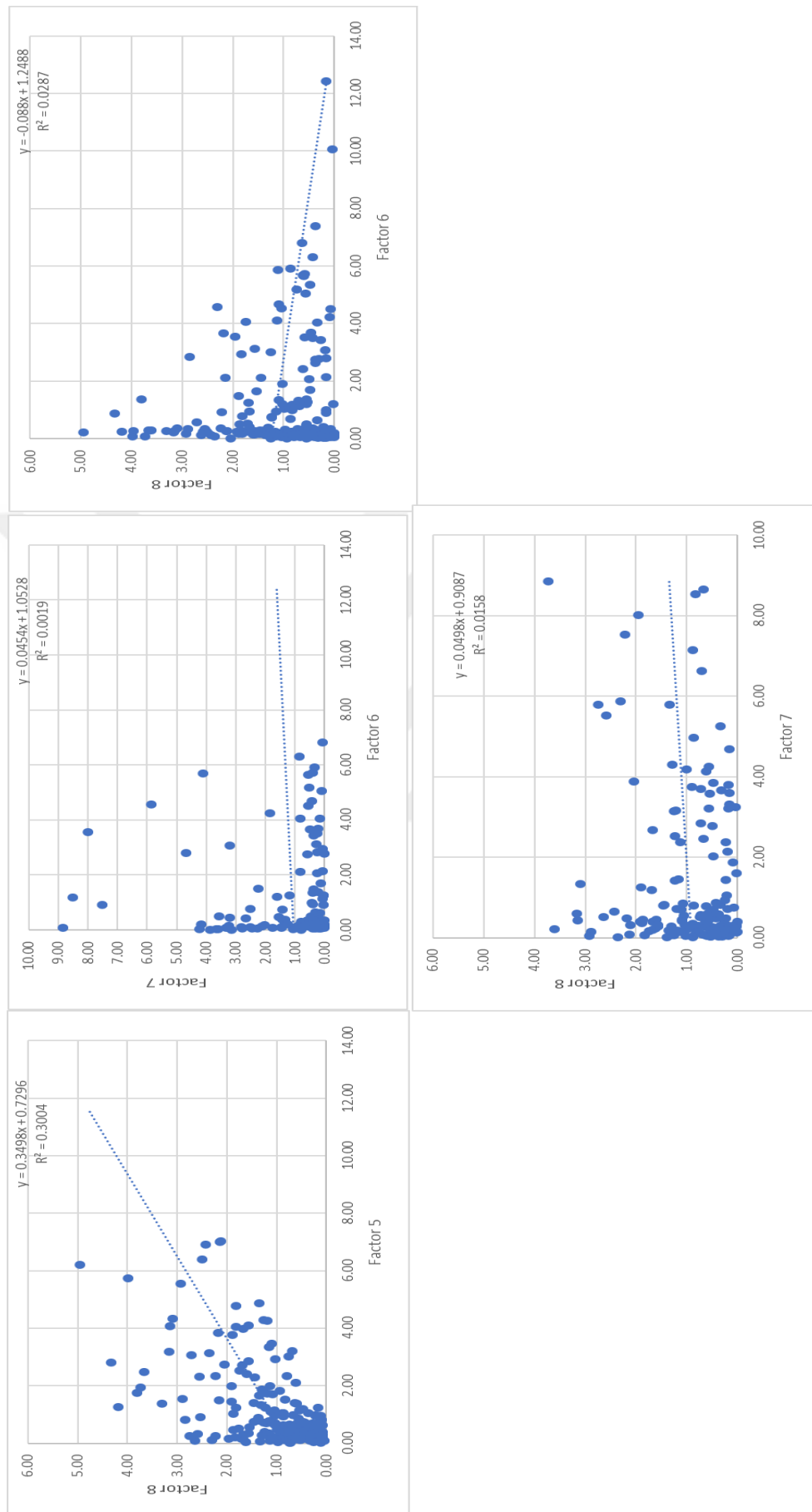


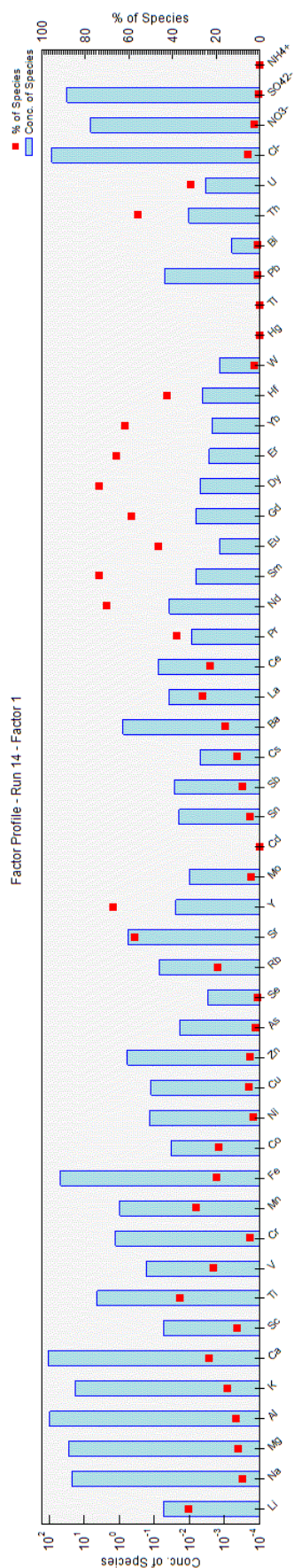
Figure 4.56. G space plots of factors for the PM_{2.5} analysis (continued)

with the median values of the parameter which is uploaded to the programme (Table 4.13). The ratios were close to unity except for Sr, Y, La, Ce, Pr, Nd, Sm, SO_4^{2-} . Therefore, the predicted concentrations were similar with the observed concentrations.

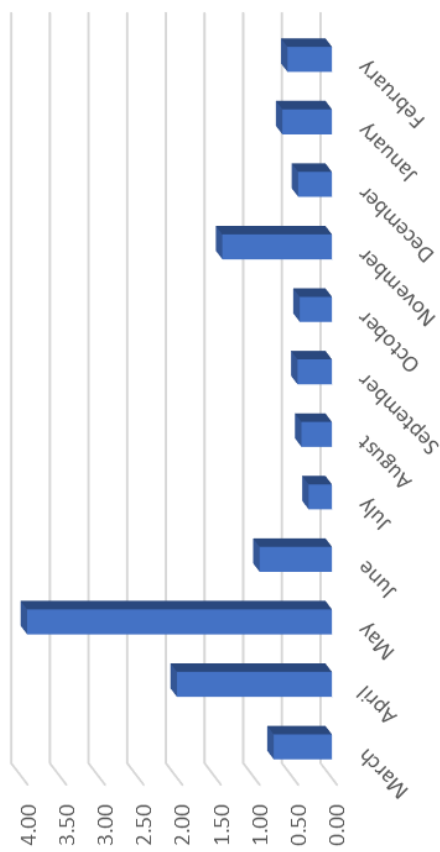
Table 4.13. The relationships of predicted concentrations by PMF and observed median concentrations of parameters (ng.m^{-3})

	Predicted	Observed	Predicted/ Observed		Predicted	Observed	Predicted/ Observed
Li	0.166	0.146	1.13	Cs	0.0314	0.0422	0.74
Na	273	289	0.94	Ba	4.91	4.56	1.08
Mg	272	277	0.98	La	0.149	0.0581	2.57
Al	898	898.	1.00	Ce	0.341	0.109	3.13
K	123	117	1.05	Pr	0.0233	0.0102	2.28
Ca	462	429	1.08	Nd	0.0531	0.0303	1.75
Sc	0.518	0.609	0.85	Sm	0.00866	0.00521	1.66
Ti	11.7	9.76	1.20	Eu	0.00290	0.00245	1.18
V	0.785	0.800	0.98	Gd	0.0108	0.00739	1.46
Cr	26.7	31.3	0.85	Dy	0.00674	0.00464	1.45
Mn	3.39	2.97	1.14	Er	0.00407	0.00243	1.68
Fe	240	249	0.96	Yb	0.00375	0.00246	1.52
Co	0.175	0.141	1.24	Hf	0.0101	0.00865	1.17
Ni	4.36	3.15	1.38	W	0.0484	0.0821	0.59
Cu	2.53	2.30	1.10	Hg	0.0278	0.0342	0.81
Zn	12.3	11.8	1.04	Tl	0.0377	0.0335	1.13
As	0.956	0.810	1.18	Pb	3.97	3.66	1.08
Se		0.344	0.00	Bi	0.0625	0.0434	1.44
Rb	0.341	0.348	0.98	Th	0.0184	0.0133	1.39
Sr	2.14	0.709	3.03	U	0.0107	0.00808	1.33
Y	0.0863	0.0225	3.84	Cl⁻	1443	1672	0.86
Mo	0.175	0.281	0.62	NO₃⁻	256	186	1.38
Cd	0.0327	0.125	0.26	SO₄²⁻	5276	2186	2.41
Sn	0.440	0.423	1.04	NH₄⁺	2045	2178	0.94
Sb	0.229	0.323	0.71				

Figure 4.57 illustrates results of Factor 1. In this factor, soil elements like Sr, Y, Pr, Nd, Sm, Dy, Er, and Yb were highly observed (higher than 60%). Titanium, Li, Mn, La, Ce, Pr, Hf, Th, U were explained 40% and Al, Mg, Na, Ca, V, Fe, Co, Rb, were observed below 30%. This indicated soil factor contribution. However, G scores



Factor 1



Factor 1

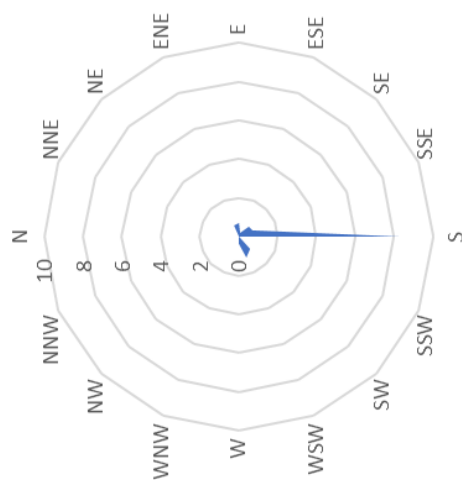


Figure 4.57. PMF results of Factor 1 for PM_{2.5}

increases in March, April, and May 2013, this supported the transport from Saharan dust. Daily variations of G scores are illustrated in Figure 4.58. Antimony, Cr, and Se were moderately enriched in the factor (Figure 4.59) which showed long range transportation. The lowest G scores observed in July 2013. There was an increase in 24.11.2013. The back trajectories which had the greater G scores were drawn. All trajectories incidated also the Saharan dust factor (Figure 4.60).

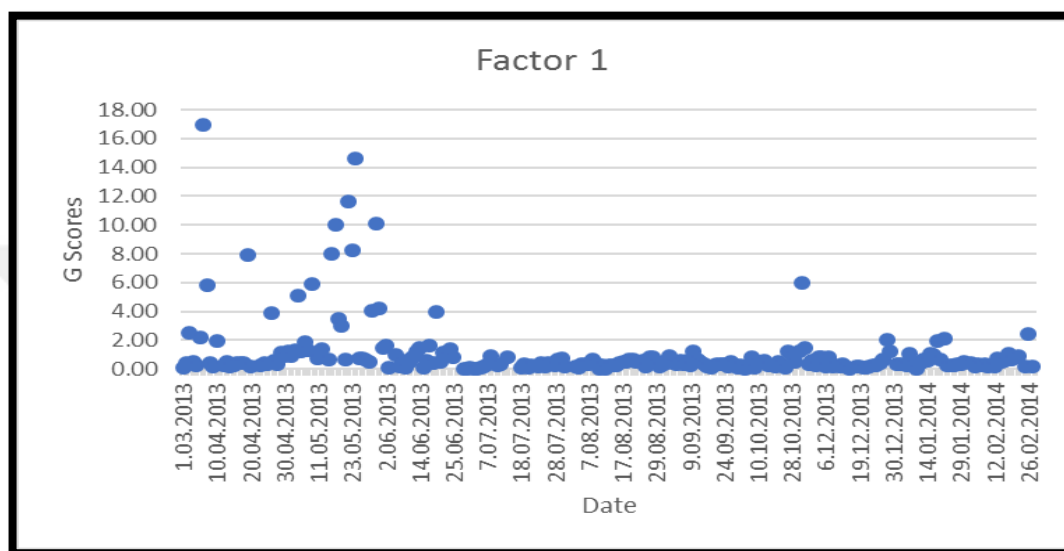


Figure 4.58. Daily variations of G-scores for Factor 1 in PM_{2.5}

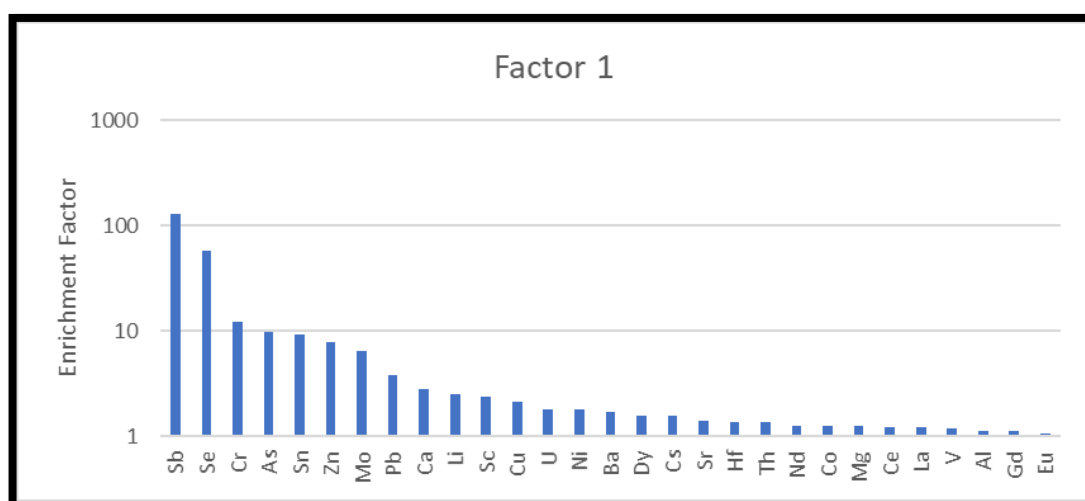


Figure 4.59. The enrichment factor values in Factor 1 for PM_{2.5}

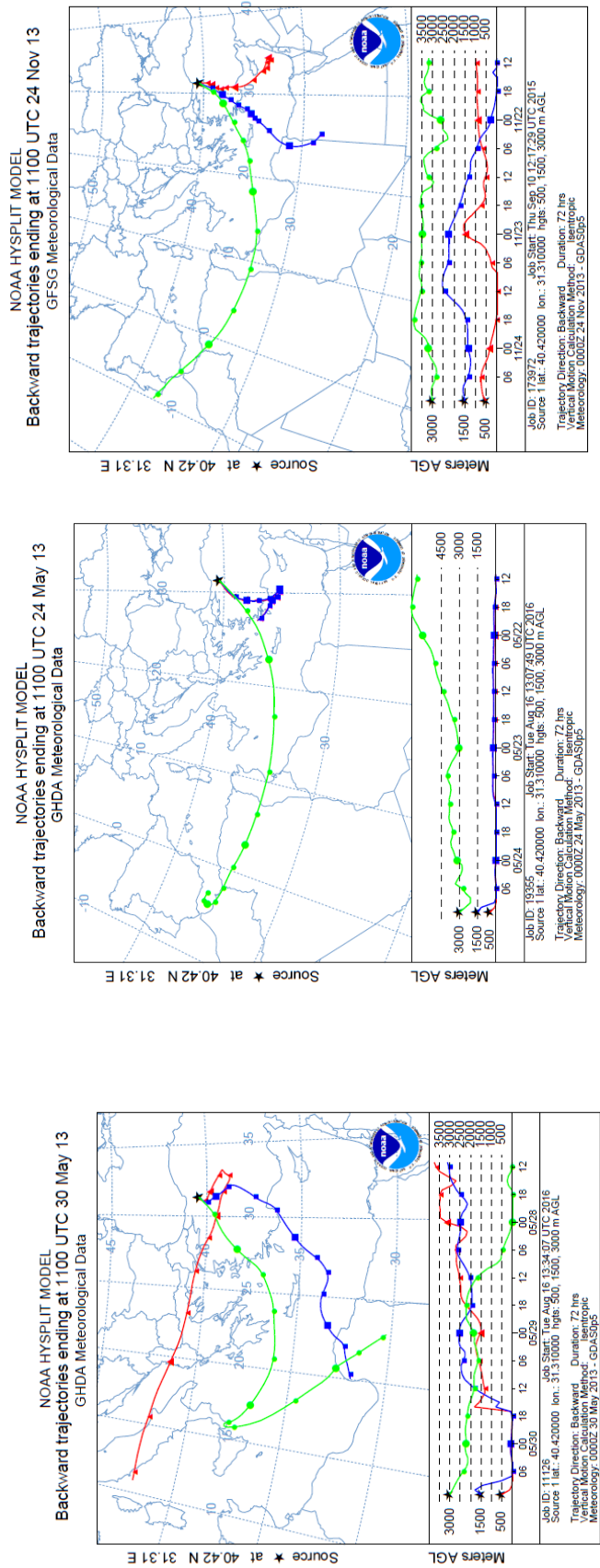


Figure 4. 60. The back trajectories of dates which had higher G score For Factor 1in PM_{2.5}

Figure 4.62. illustrates the results of factor 2. In this factor, NO_3^- , K, V, Ba, As, Se, Cd, Sn, Sb, Pb, were explained. Whereas NO_3^- was observed nearly 80%, The percent contribution of K, V, As, Se, Sn, Sb, Ba, W, Pb were nearly 20%. Vehicles mainly emit $\text{PM}_{2.5}$ from the exhaust pipe (Ferm and Scöberg, 2015) and NO_x are the most emitted tracers. Brake and type wear of vehicles also emit the elements like As, Se, Mn, Fe, Ba, Cu, Zn, Cd, and Cr (Harrison and Thorpe, 2008). G scores were greater in April and in September. Daily variations were also evaluated and some days in February had also higher G scores than the other winter days (Figure 4. 61). Selenium, Sb, As, Cd, Sn, Pb, Zn, Cr, and W were highly enriched whereas Cu, Ba, Sc, Ca, and V were moderately enriched in the factor 2 (Figure 4.63). The dominant wind sectors were West and West South West and East South East. TEM and D-100 highways were East South East sector. The air masses came from Russia also affected the factor (Figure 4.64). Those indicated mixed urban contribution to $\text{PM}_{2.5}$.

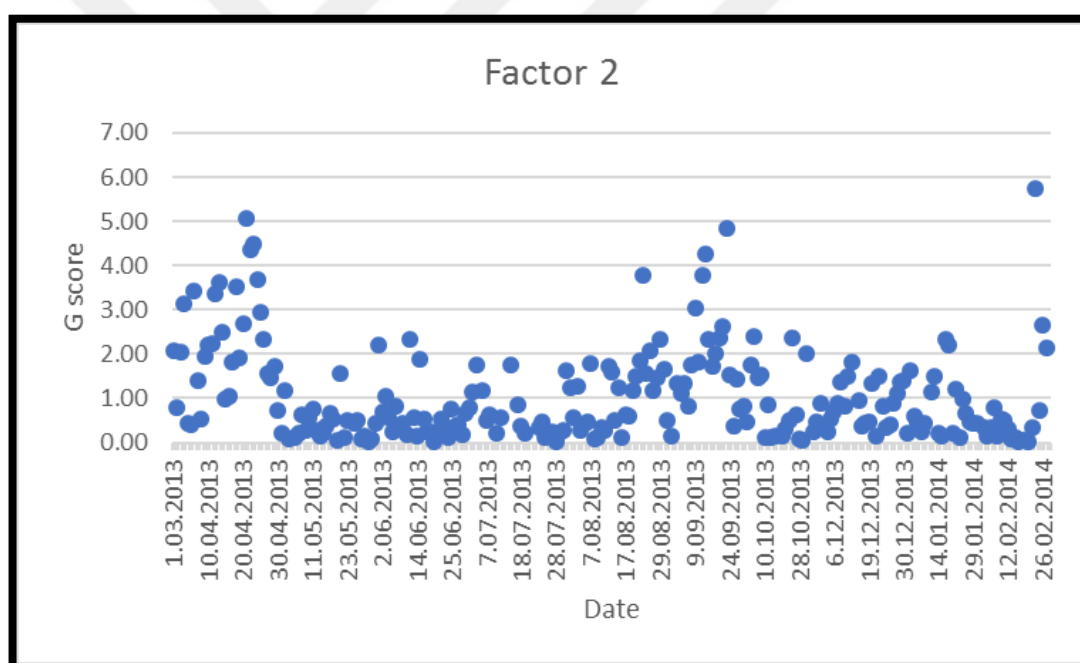


Figure 4.61. Daily variations of G scores for Factor 2 in $\text{PM}_{2.5}$

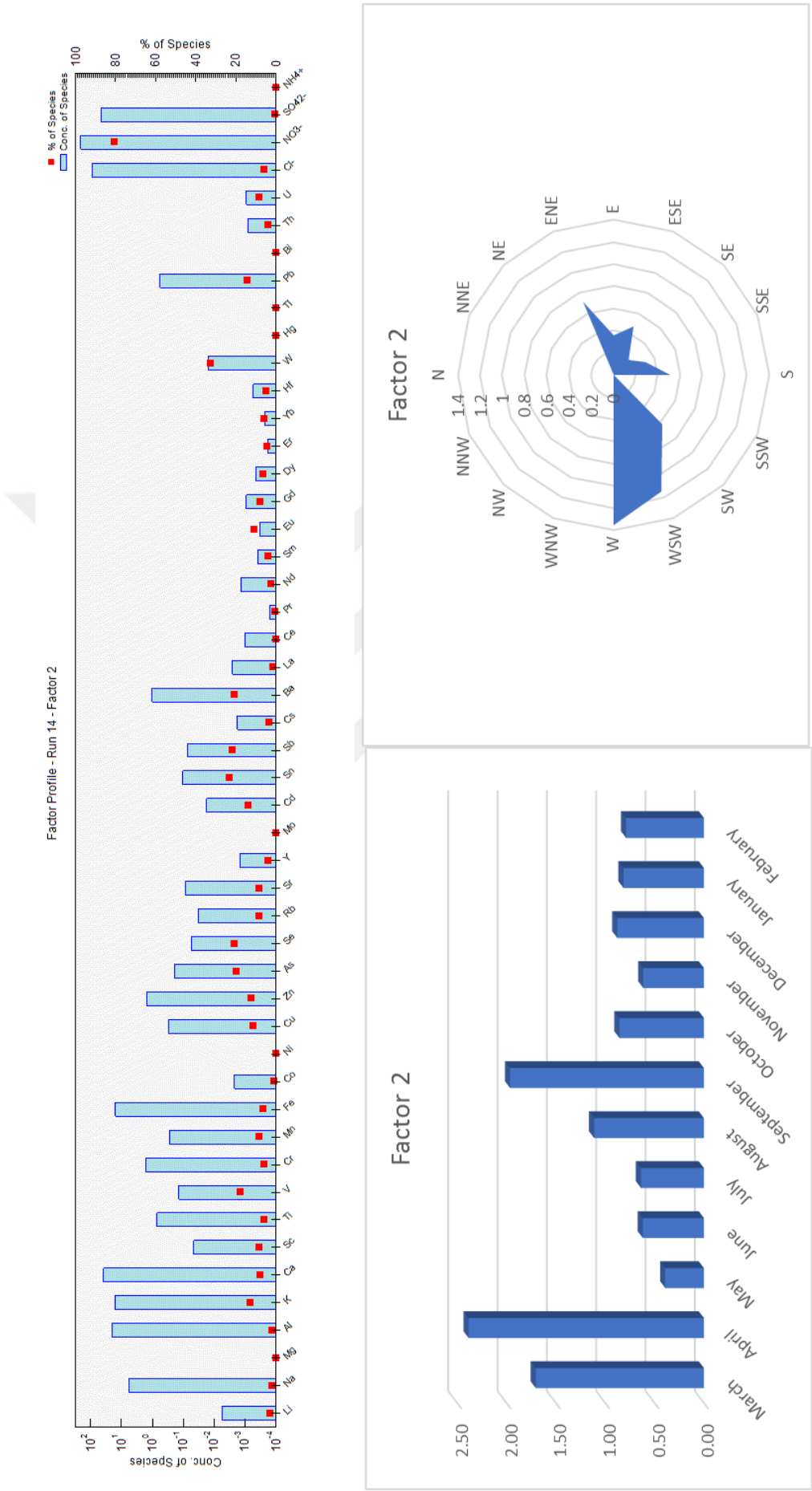


Figure 4.62. PMF results of Factor 2 for PM_{2.5}

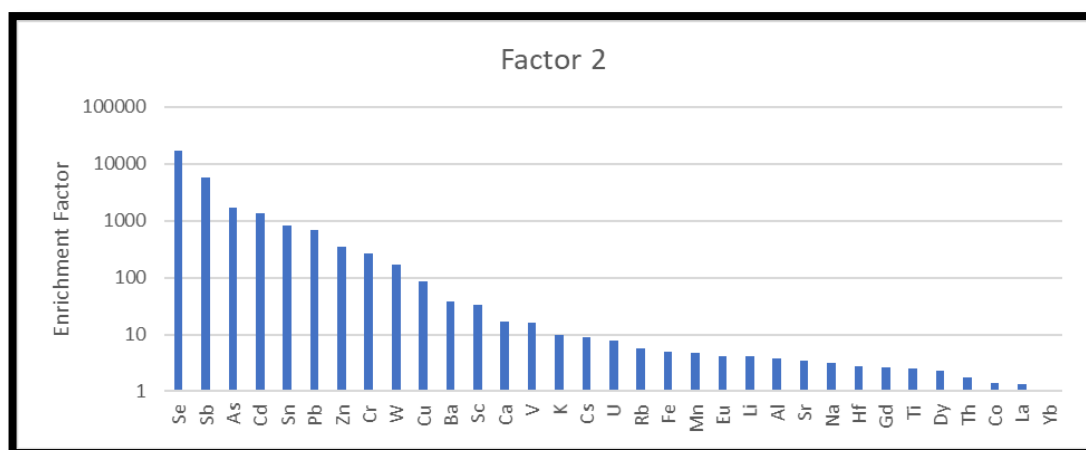


Figure 4.63. The enrichment factor values in Factor 2 for PM_{2.5}

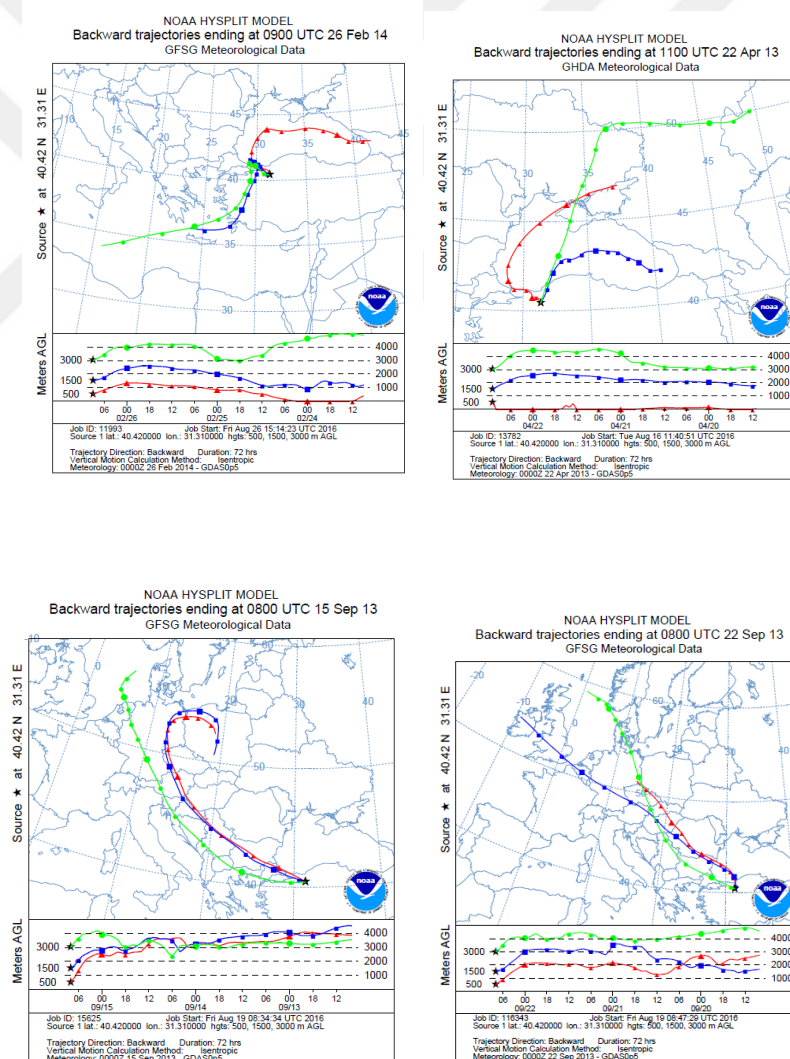


Figure 4.64. Back Trajectories of dates which had the highest G scores for Factor 2 in PM_{2.5}

In Factor 3, Na, Mg, Al, Ca, Sc, Ti, Cr, Fe, Ba, Hg and Cl^- were explained in greater extend (higher than 40%). Contribution of marine aerosols from Black Sea was seen. Antropogenic elements like Ni, Cu, Zn, Mo, Sn were also observed (nearly 40%). This indicated the industrial activites. The monthly G scores signed the continuous sources of the factor in whole year (Figure 4. 65). In the factor, highly enriched elements were Se, Hg, Cr, Sn, Zn, Mo, Ni, Sc, As, and Cu (Figure 4.66). The back trajectories also support the identification of sea and industrial activities with long range transport from Europe-Russia and central Anatolia (Figure 4.67). G score wind sector analysis also signed sand quarries around the sampling area coming from ENE and ESE sectors (Figure 4.68).

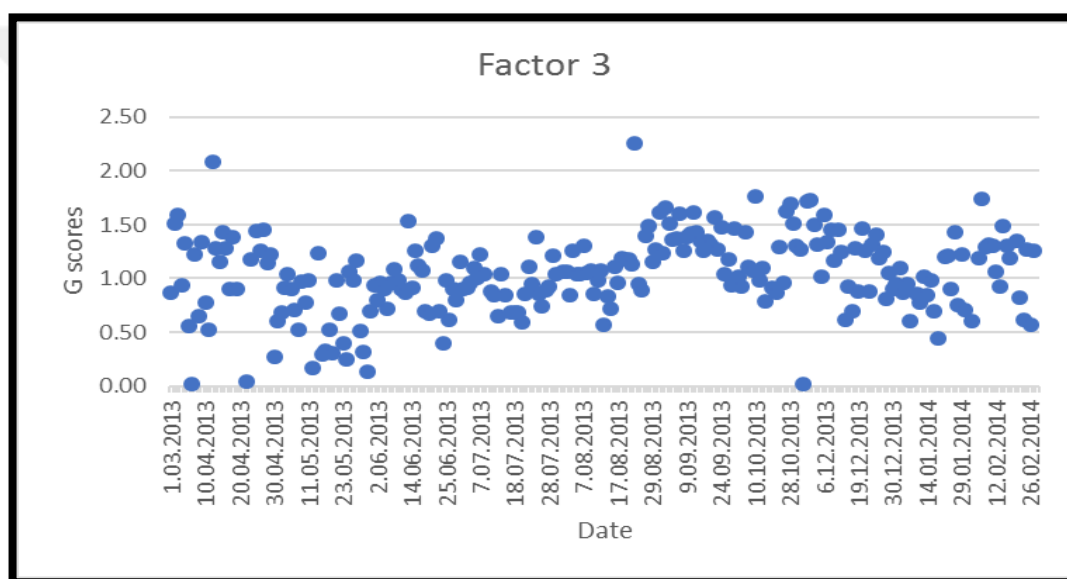


Figure 4.65. Daily variations of G scores for Factor 3 in $\text{PM}_{2.5}$

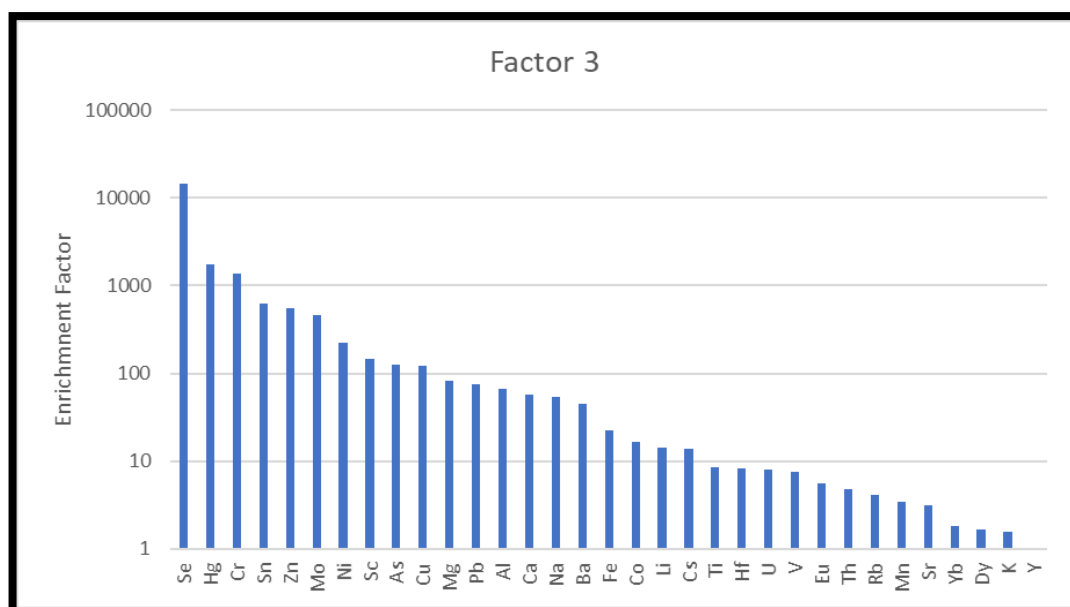


Figure 4.66. The enrichment factor values in Factor 3 for PM_{2.5}

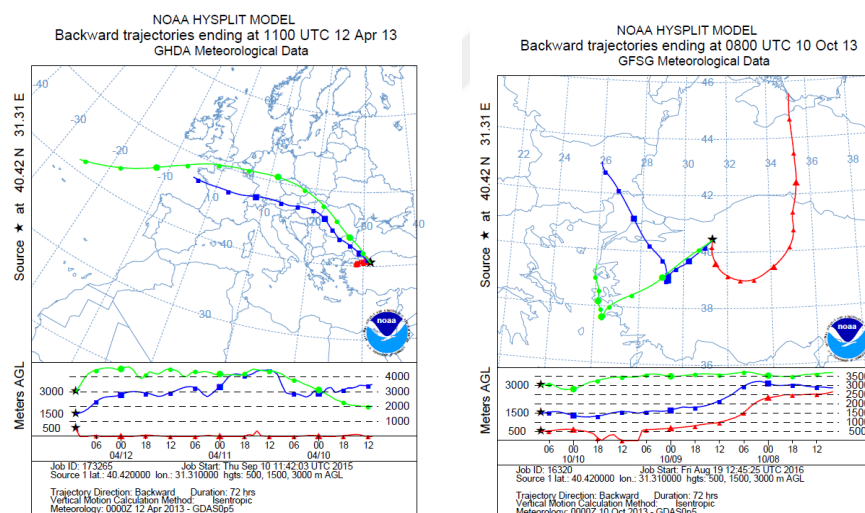
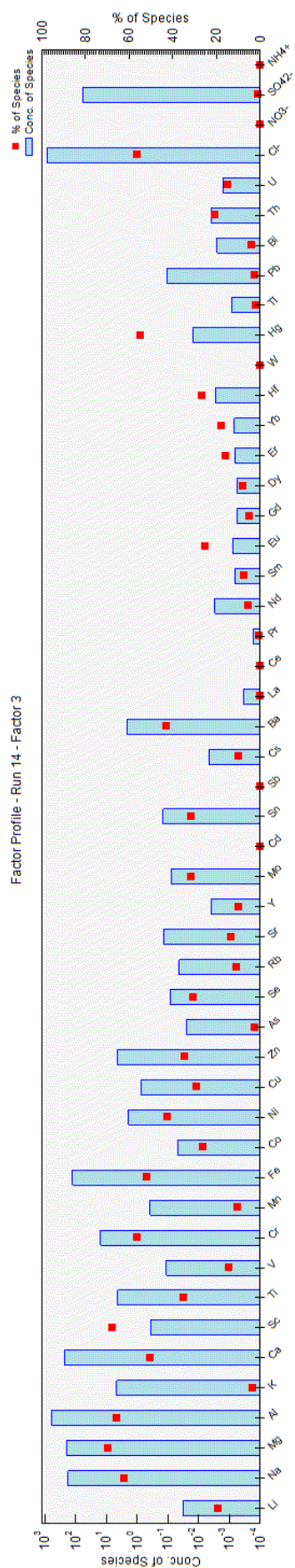
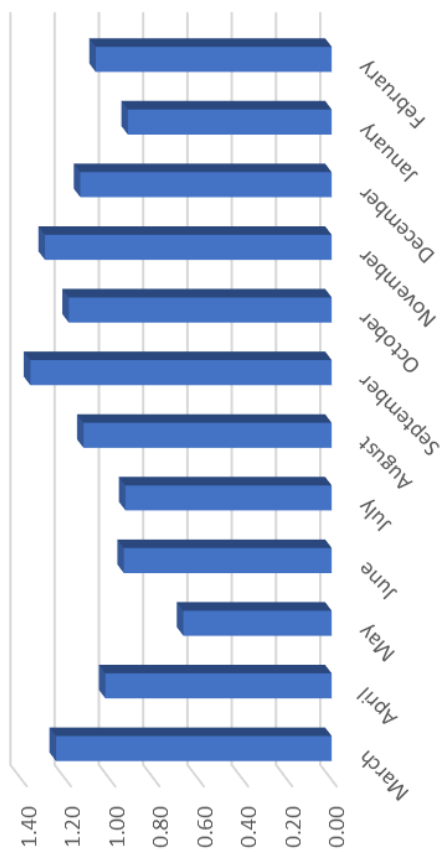


Figure 4.67. Back trajectories of the date highest G score belongs to Factor 3 for PM_{2.5}



Factor 3



Factor3

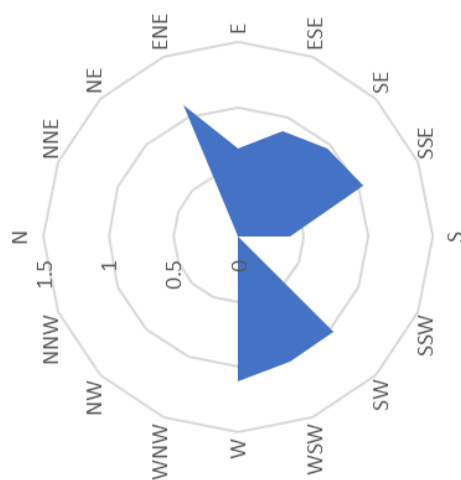


Figure 4.68. PMF results of Factor 3 for PM_{2.5}

Figure 4.71 illustrates the results of Factor 4. In this factor, NH_4^+ and Cl^- were highly observed. NH_4^+ was observed in the greatest percentage (80%) and this indicated the effect of poultry sector. G scores increased in the months (spring and summer seasons) in which agricultural activities were very high. Because there were usages of natural chicken fertilizer around the sampling area. 28/06/2013 had the highest G scores (Figure 4.69). Selenium, Sb, Cr, and Pb were highly enriched whereas Mo, Cd, W, V, and Na were moderately enriched (Figure 4.70). In addition, poultries are mostly located in East South East direction and the air masses came from East South East sector had the highest G scores (Figure 4.71).

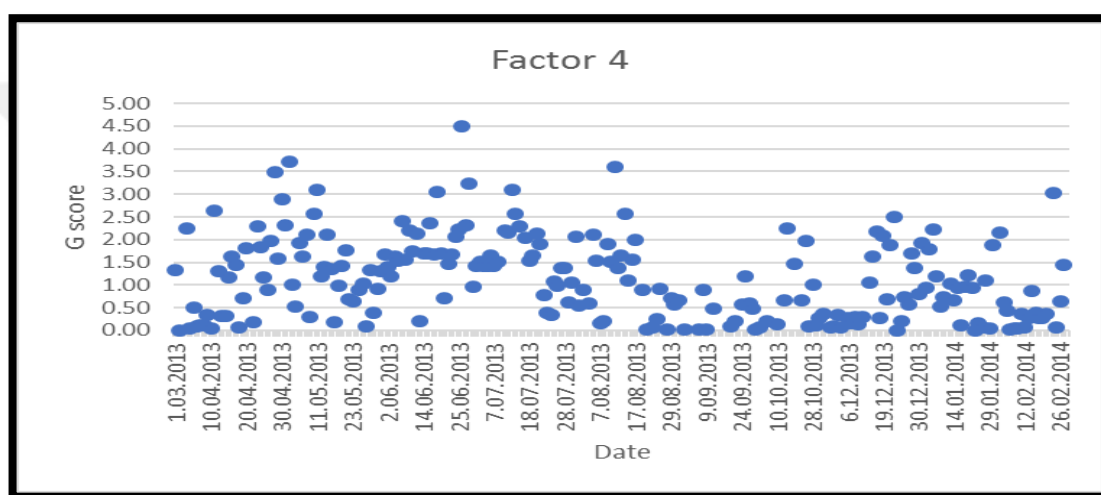


Figure 4.69. Daily variations of G scores for Factor 4 in $\text{PM}_{2.5}$

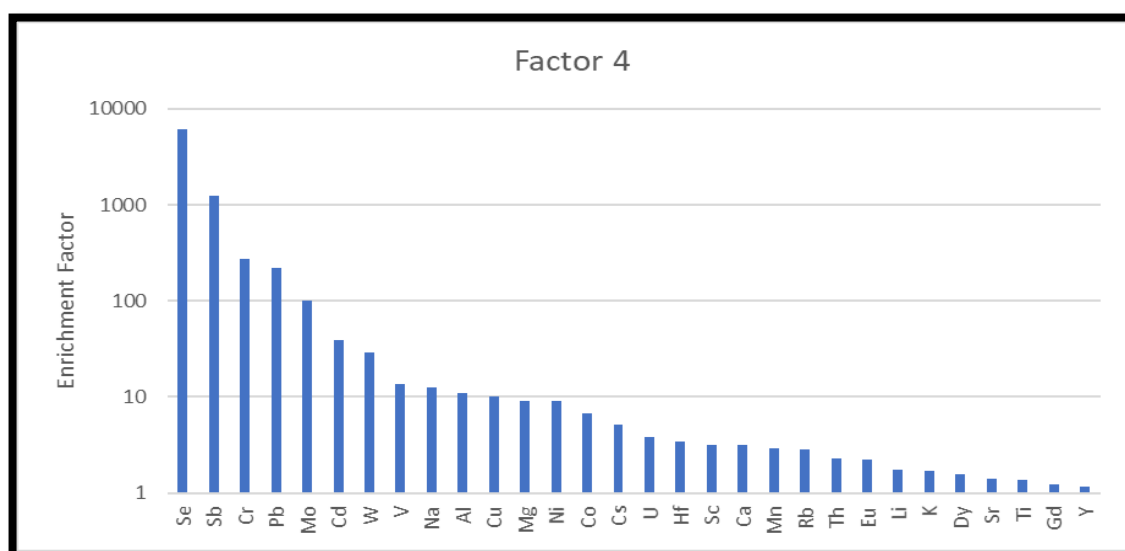


Figure 4.70. The enrichment factor values in Factor 4 for $\text{PM}_{2.5}$

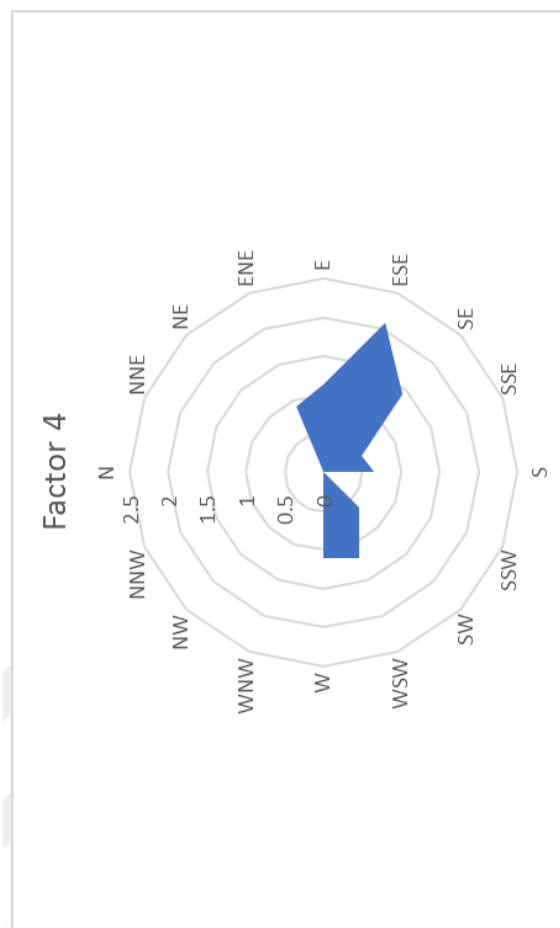
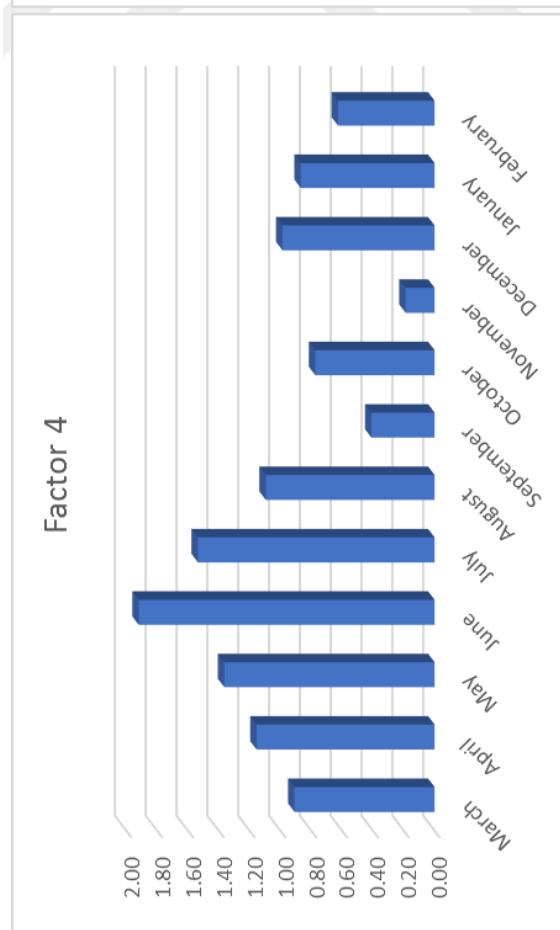
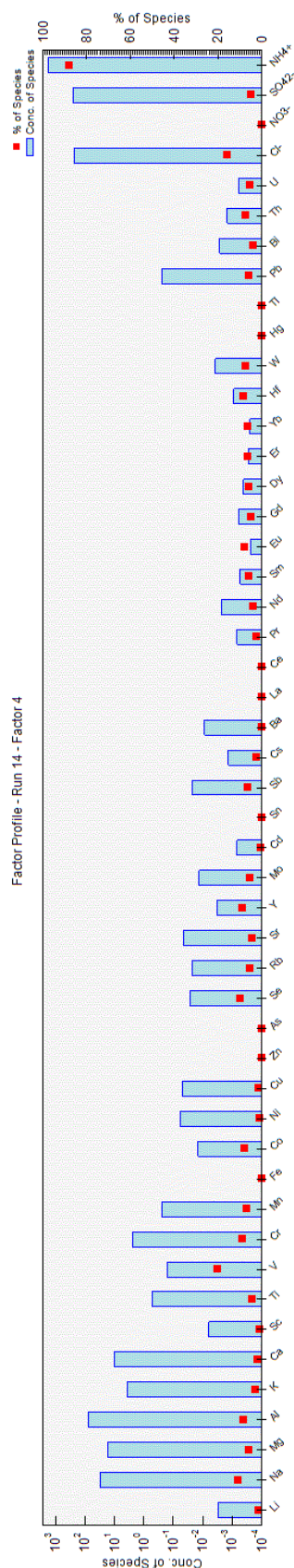


Figure 4.71. PMF results of Factor 4 for PM_{2.5}

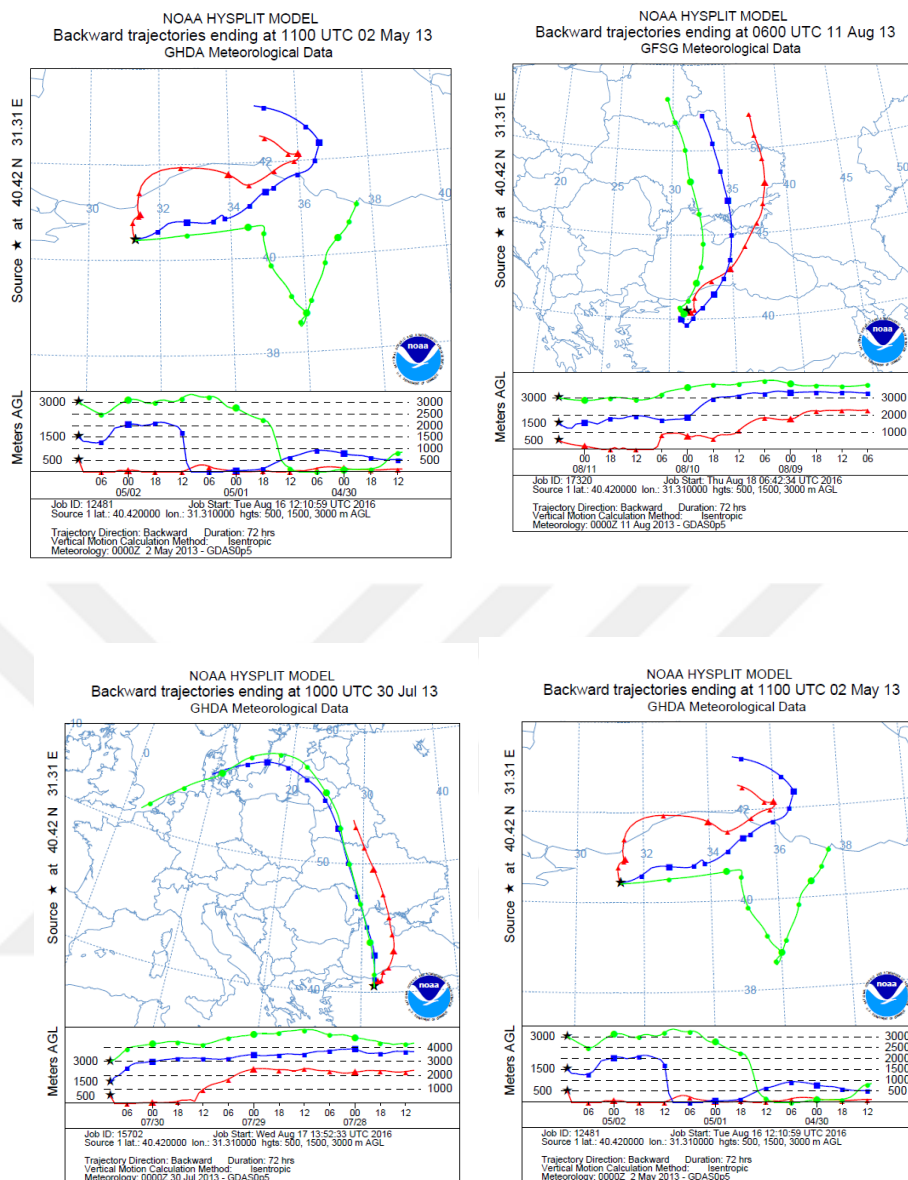


Figure 4.72. Some back trajectories examples for Factor 4 in PM_{2.5}

Figure 4.73 illustrates the results of Factor 5. In this factor, As, K, Tl, Pb, Hg, Sb, Sn, Mo and Bi were highly observed. Arsenic was observed in the greatest percentage (60%) and Bi and K was observed in 40%. Antimony, Sn, Hg, Tl, Pb, Bi and U were observed greater than 20%. Lignite is generally used for heating process and Turkish lignites have higher As concentrations (Yenisoy Karakaş, 2000). Therefore, this properties indicated coal and biomass burning. G scores increased winter months (Figure 4.74). Antimony, Se, As, Hg, and Pb highly enriched in the factor (Figure 4.75). The pollution roses of As in PM_{2.5} was support our investigation and signed the city center (ESE sector) (Figure 4.76).

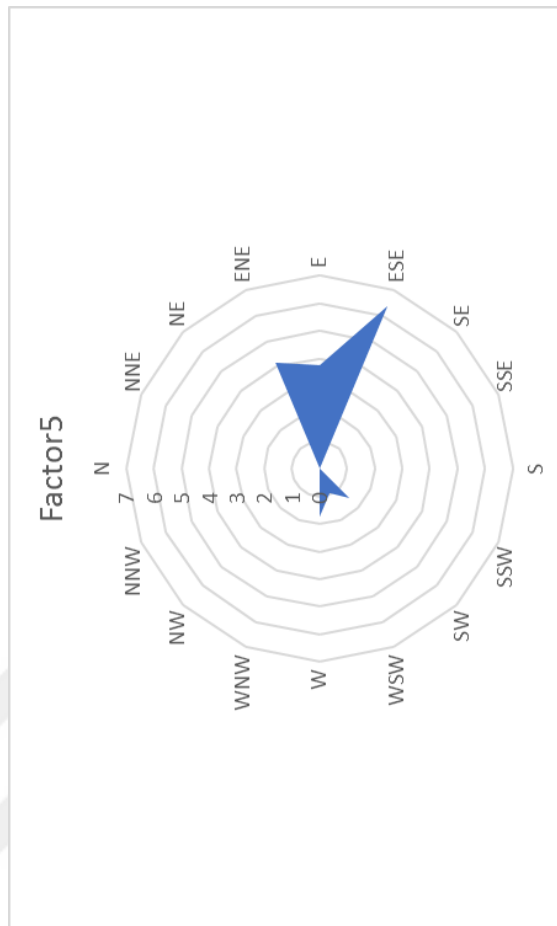
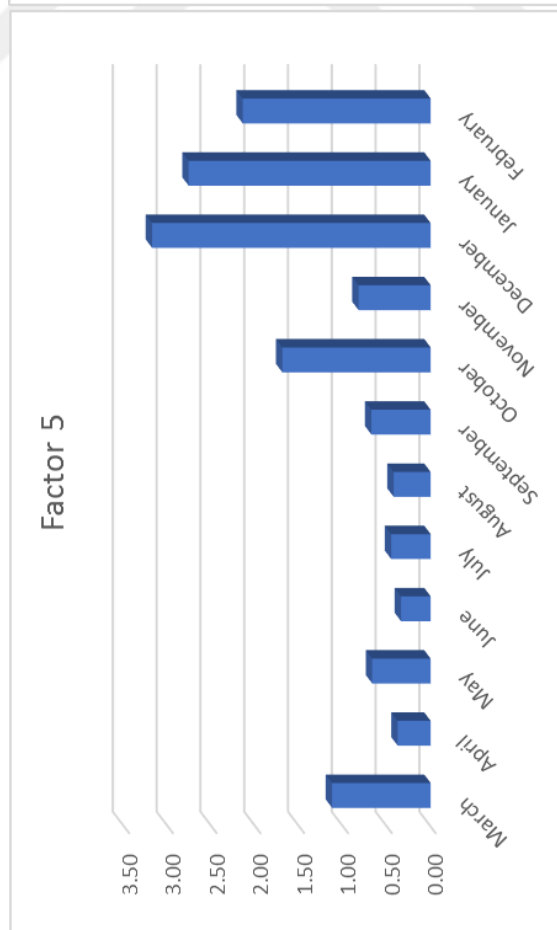
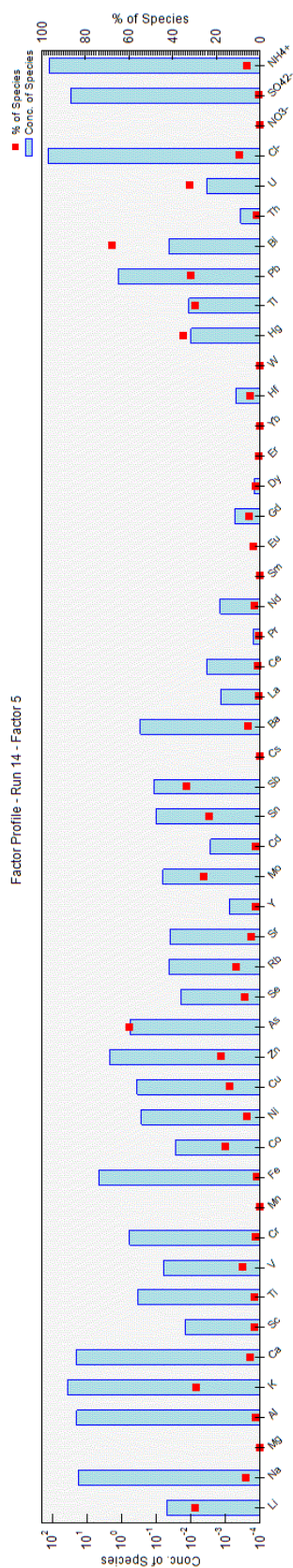


Figure 4.73. PMF results of Factor 5 for PM_{2.5}

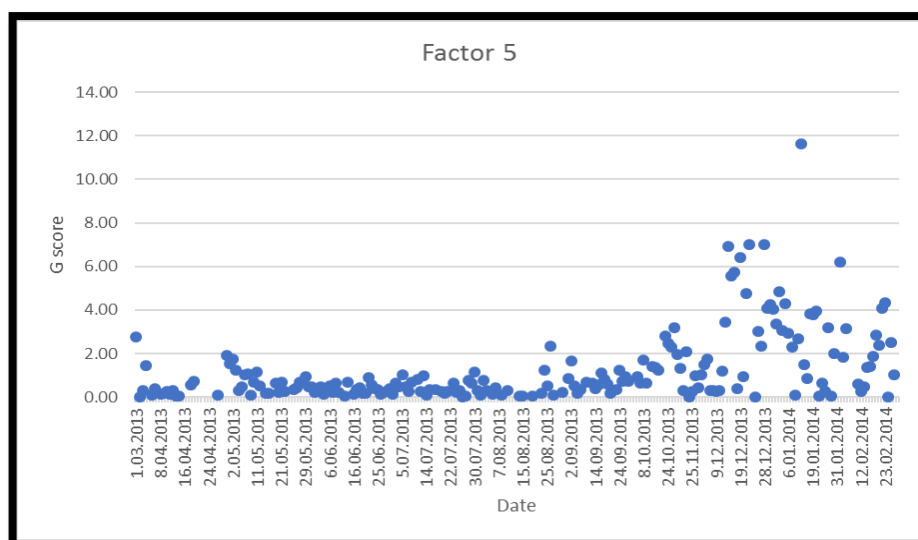


Figure 4.74. Daily variations of G scores for Factor 5 in PM_{2.5}

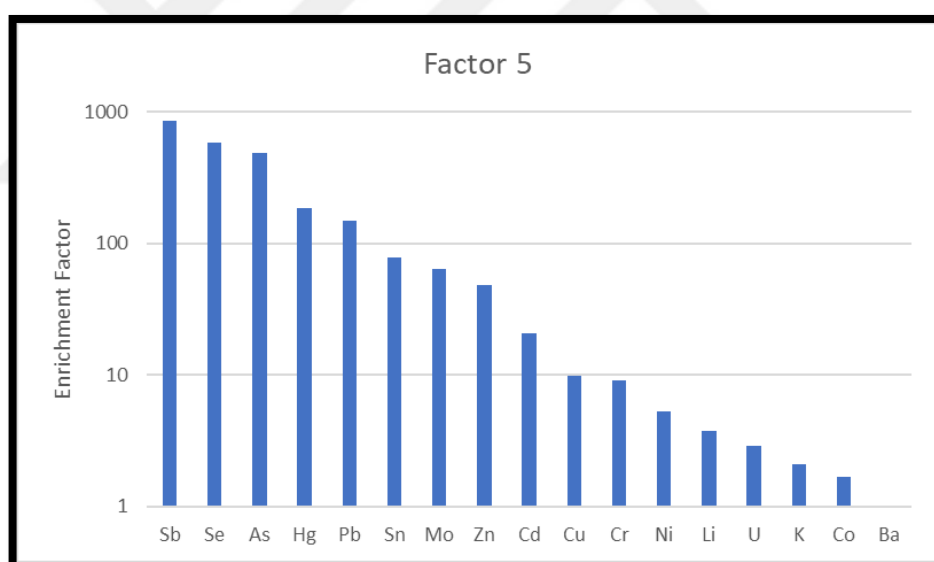


Figure 4.75. The enrichment factor values in Factor 5 for PM_{2.5}

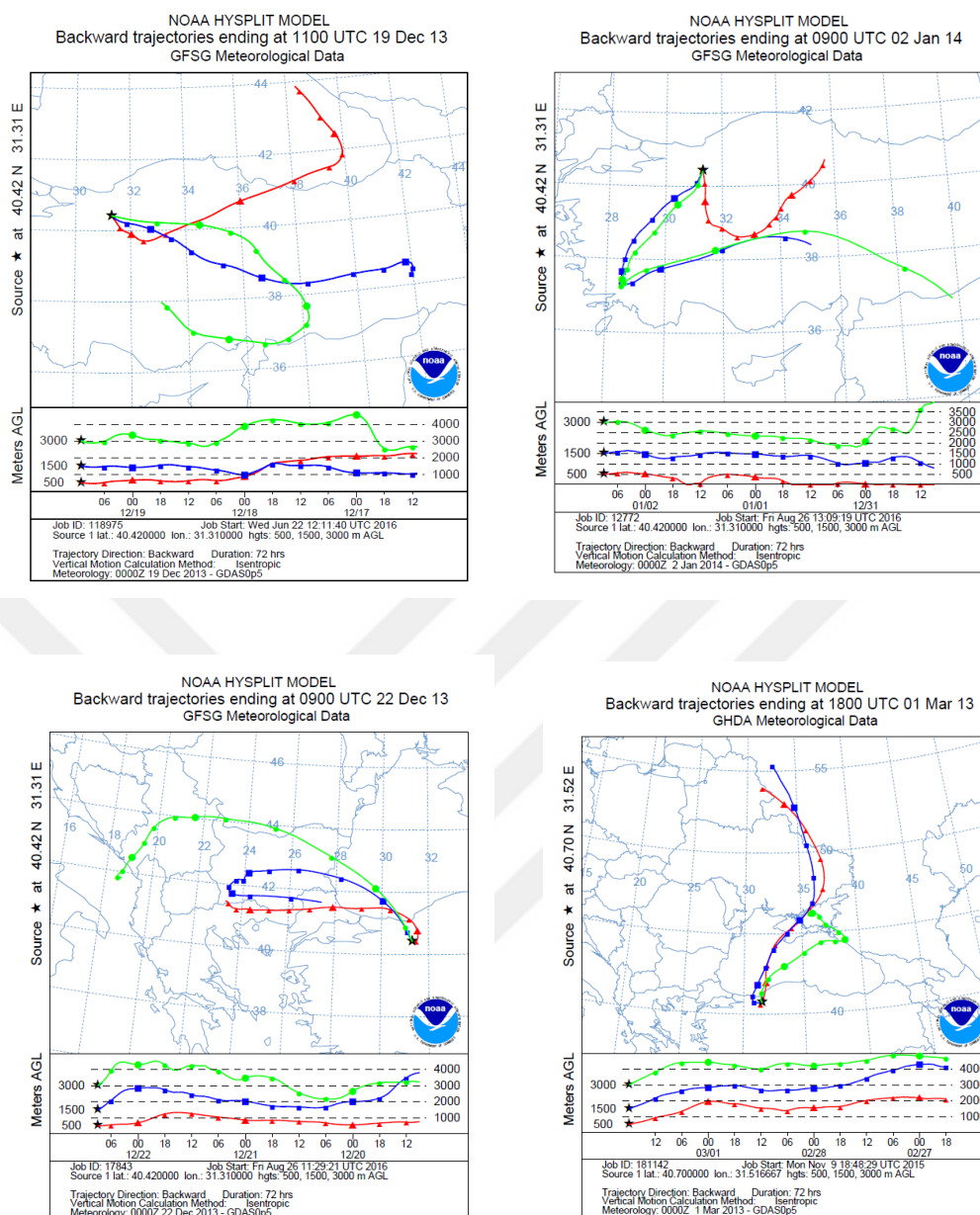


Figure 4.76. Some examples of back trajectories for Factor 5 in $PM_{2.5}$

Figure 4.77 illustrates the results of Factor 6. In this factor, La, Ce, Pr, Nd, Co, Ni, Cu, Mn, Mo, Cd were observed. La, Ce and Pr were explained greater than 60%. Lanthanum and Ce are used in automobile gasoline. Therefore, this indicated traffic emission. The percent contributions of Mn, Co, Ni, Cu, Mo, Cd and W were nearly 40%. The back trajectories supported that the air masses came from Fe- Ni mining activities (Figure 4.78). There is a mining activities of Ni. The researchers also found new reserves in Karaçam, Eskişehir. There are also active quarries in middle Anatolia (Anonymous 5, 2017). G scores were greater in May, in June, in July 2013 and

in January 2014 (Figure 4.79). In this factor Sc was selected as a crustal element, since the concentration of Sm was given as zero in the output of the program. Cadmium, Sb, Mo, Hg, Cr, Ni, W, Pb, Cu, Sn, Ce, La were highly enriched in factor 6 (Figure 4.80). The air masses coming from the E, SE, S and SW affected the $PM_{2.5}$ concentrations. This factor was called as traffic-mining mixed factor.

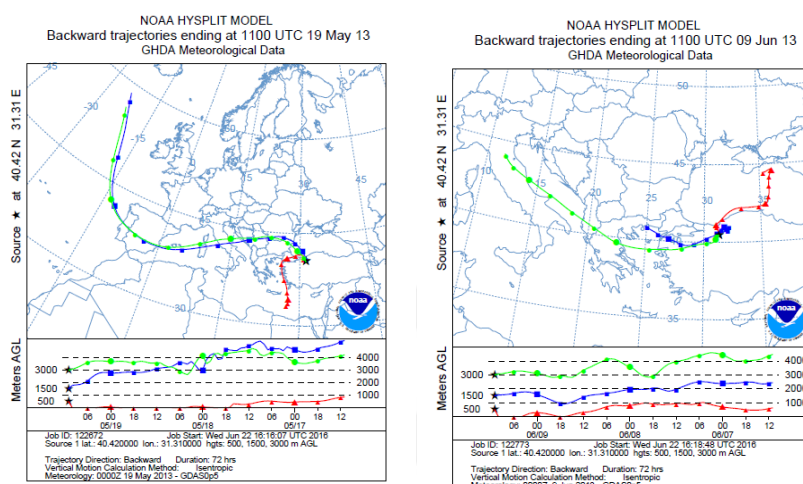


Figure 4.78. Some examples of Back trajectories of the date which had higher G scores for Factor 6 in $PM_{2.5}$

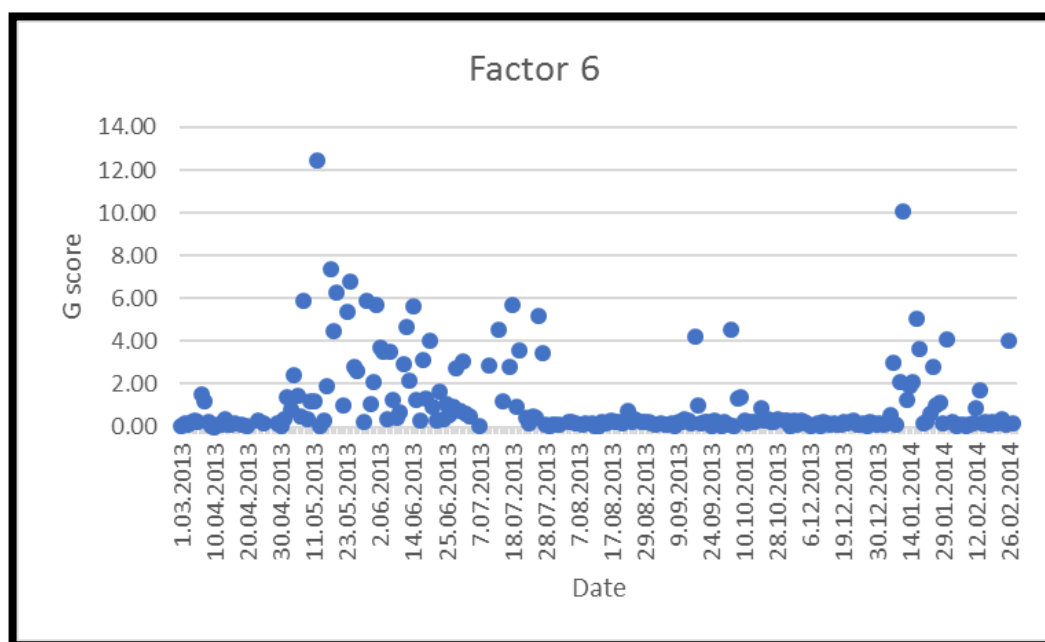


Figure 4.79. Daily variations of G scores for Factor 6 in $PM_{2.5}$

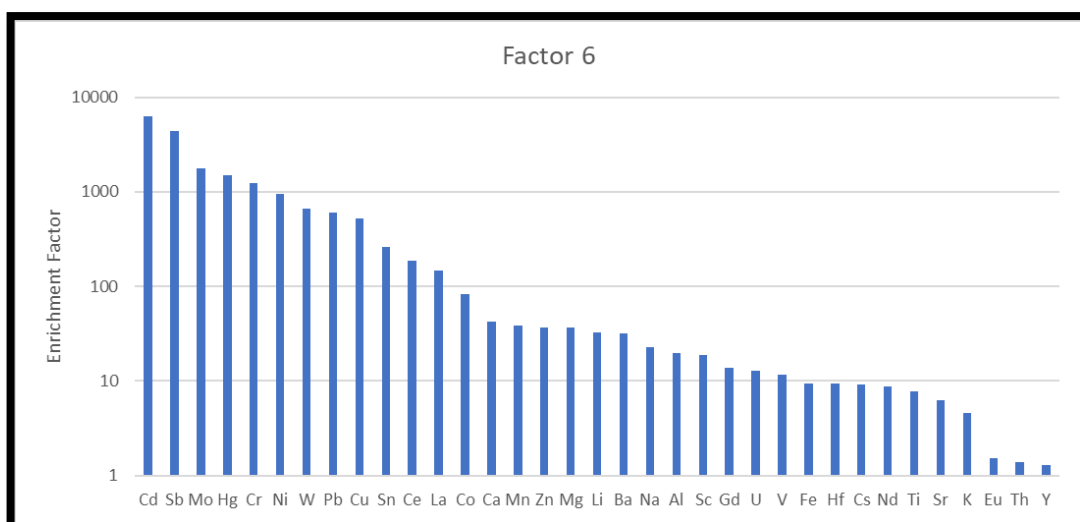


Figure 4.80. The enrichment factor values in Factor 6 for PM_{2.5}

Figure 4.82 shows the graph of Factor 7. In this factor, SO_4^{2-} was explained in 87%. Nitrate and NH_4^+ were observed nearly 10%. This property indicated secondary inorganic aerosols. Daily variations of G scores were shown in Figure 4. 81. Selenium, Cr, Cd, Pb, As, and Zn were highly enriched whereas Sn, Hg, Cu, Sc, and Cs were moderately observed in the factor (Figure 4.83). G scores were greater in July, in April and in March 2013. G score of the winter months showed a little difference between each other. The higher G score was observed in 13/07/2013. West south west sector was the dominant sector in long range transportation (Figure 4.84).

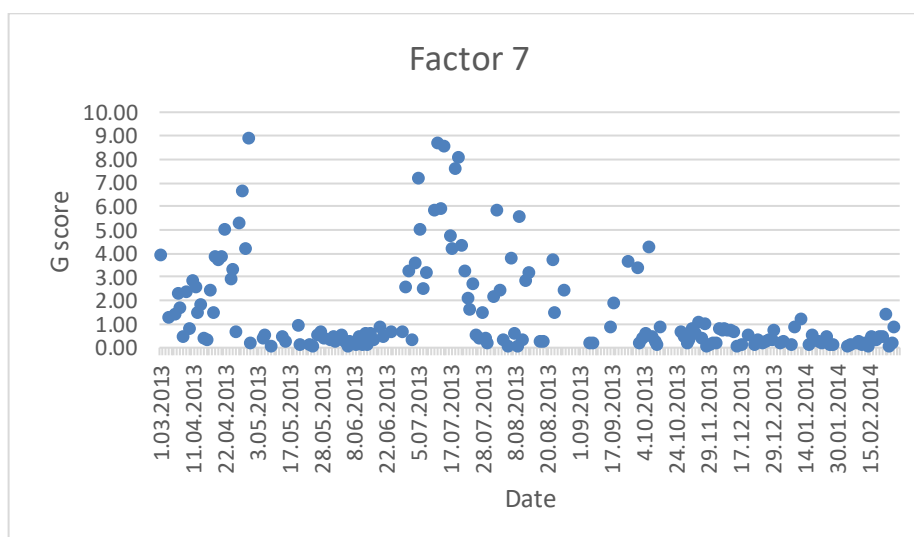


Figure 4.81. Daily variations of G scores for Factor 7 in PM_{2.5}

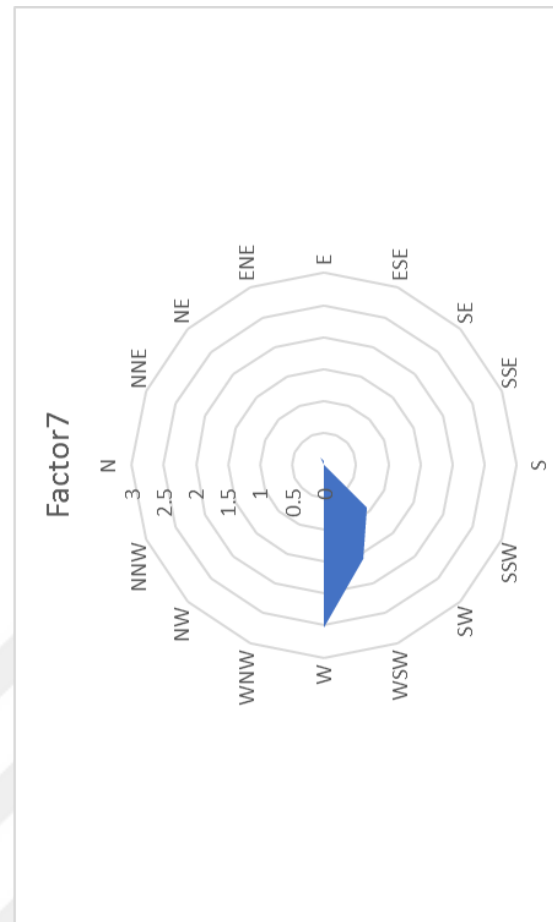
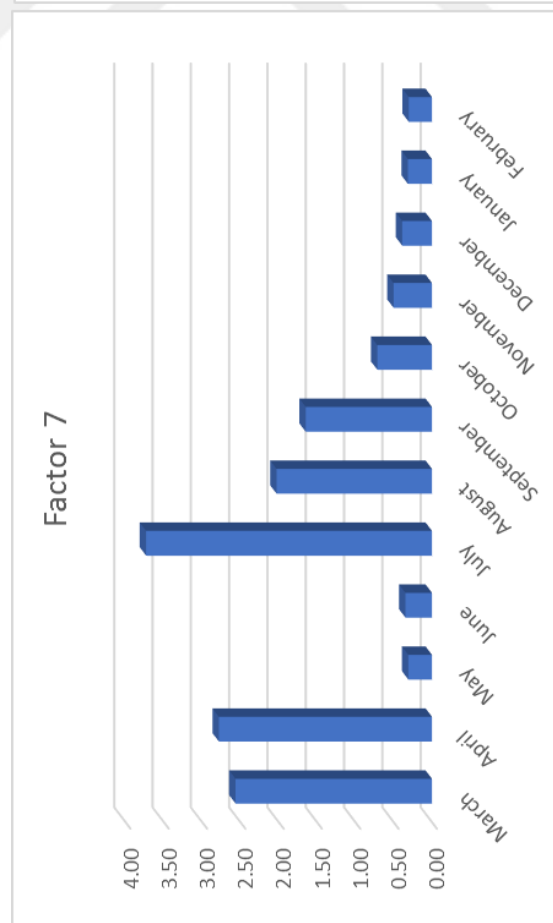
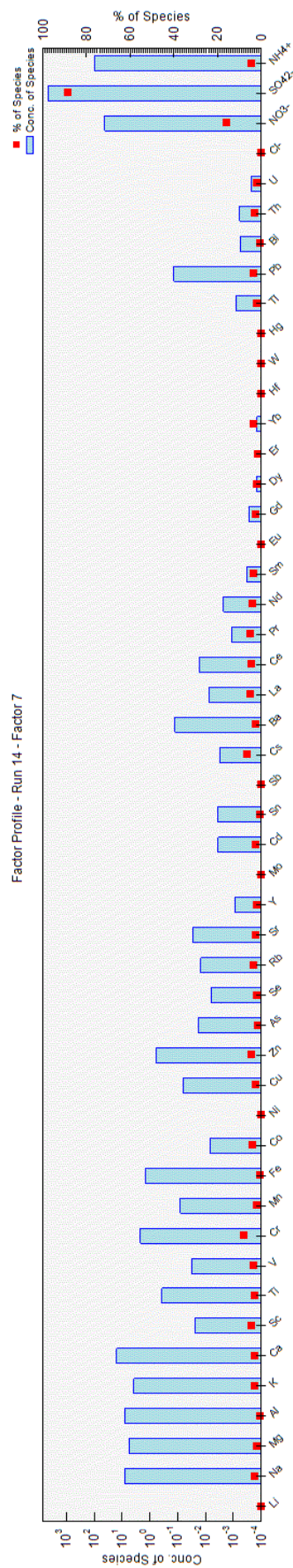


Figure 4.82. PMF results of Factor 7 results for $PM_{2.5}$

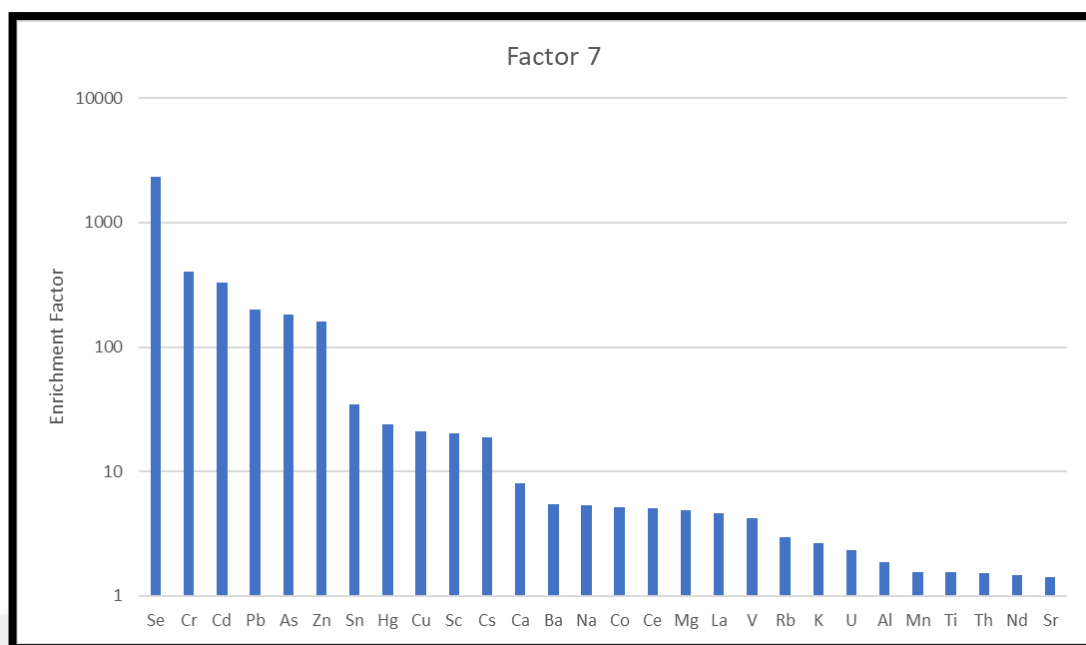


Figure 4.83. The enrichment factor values in Factor 7 for PM_{2.5}

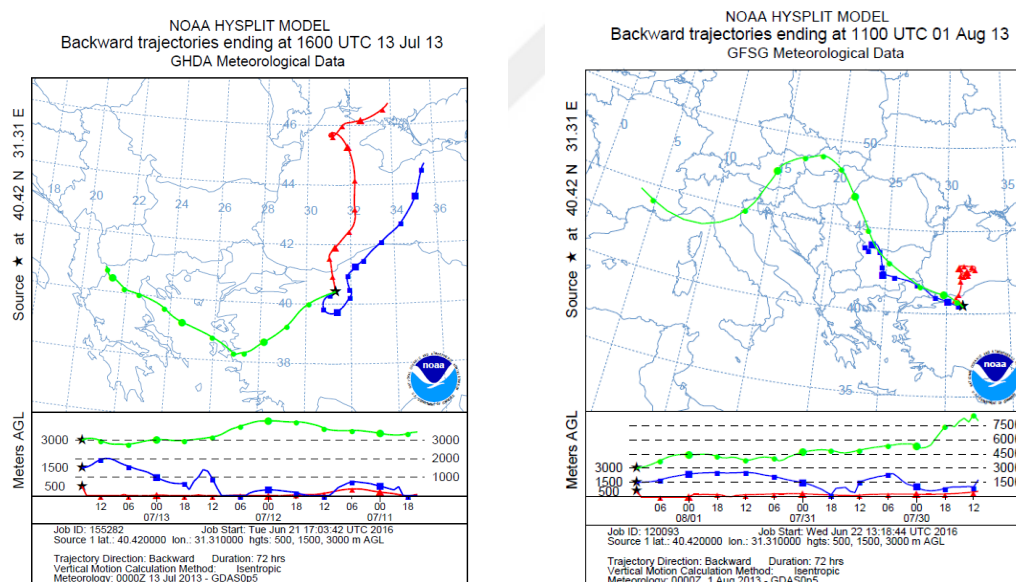


Figure 4.84. Some back trajectories of the date which has higher G scores for Factor 7 in PM_{2.5}

Figure 4. 87. illustrates the results of factor 8. In this factor, K, Mo, Fe, Ni, Cu, Zn, As, Sn, Se, Rb, Cd, Sn, Sb, Co, Cs, Tl, Pb, Bi and W were observed. Cobalt, Tl, Cd, Rb, As, Se, Sb, and K had the greatest percent contributions (higher than 40%). Potassium and Sb is the tracer of garbage burning (Christian et al., 2010). Vanadium, Mn, Fe, Cu, Zn were explained higher than 20%. Selenium, Sb, Cd, Pb, As, Zn, Sn, Mo, Cs, Cr, Ni, and Cu were highly enriched in the factor (Figure 4. 85). Antimony is the tracer element for the waste burning. There is a waste incinerator unit in the cement factory which is located at the east of the sampling point. G scores were greater in October 2013. November 2013 had the lowest G (Figure 4.86). The back trajectories showed that the air masses came from Karabük (iron-steel factory) (Figure 4.88). The elements Fe, Mn, Sb, Rb are the tracer elements of iron-steel works. The factor was named as waste incineration-iron steel factory. The effect of the center was shown in the back trajektories.

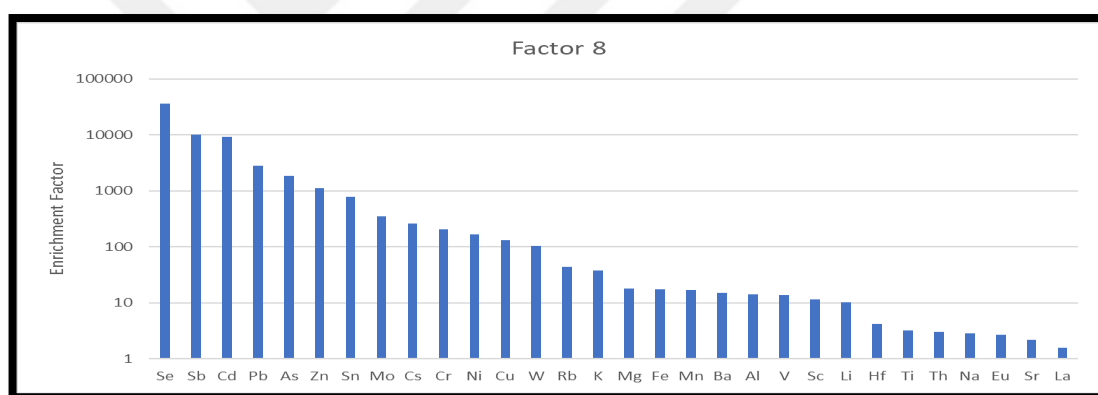


Figure 4.85. The enrichment factor values in Factor 8 for PM_{2.5}

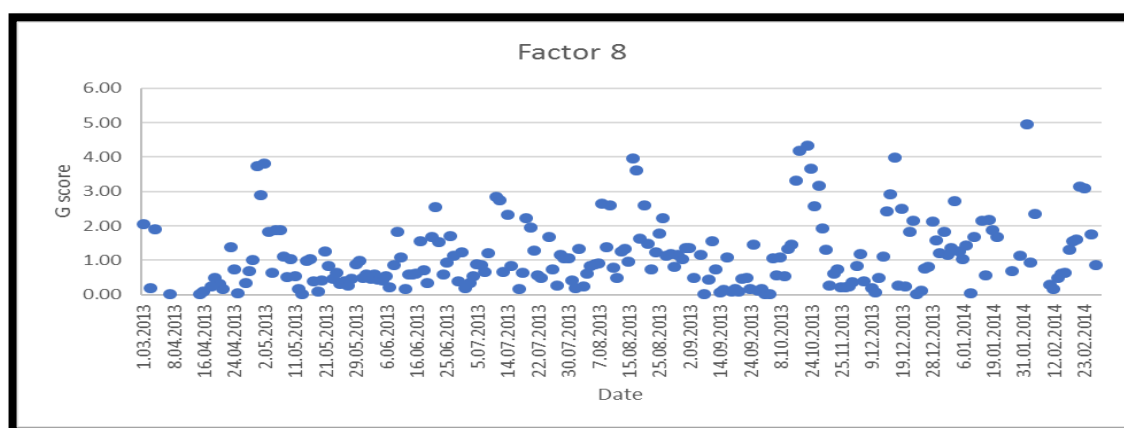


Figure 4.86. Daily variations of G scores for Factor 8 in PM_{2.5}

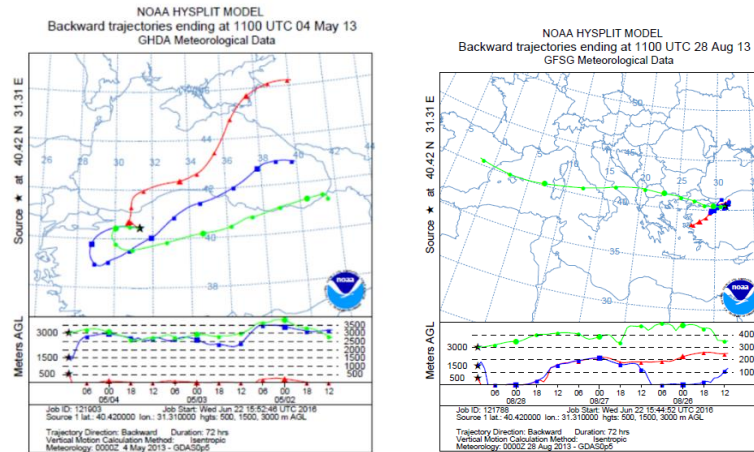


Figure 4.88. Some examples of back trajectories for Factor 8 in $PM_{2.5}$

Figure 4.89 shows the percent contribution of each factor in $PM_{2.5}$. The highest contribution belongs to industrial activities and Saharan dust factor. The lowest contribution belongs the secondary inorganic aerosols.

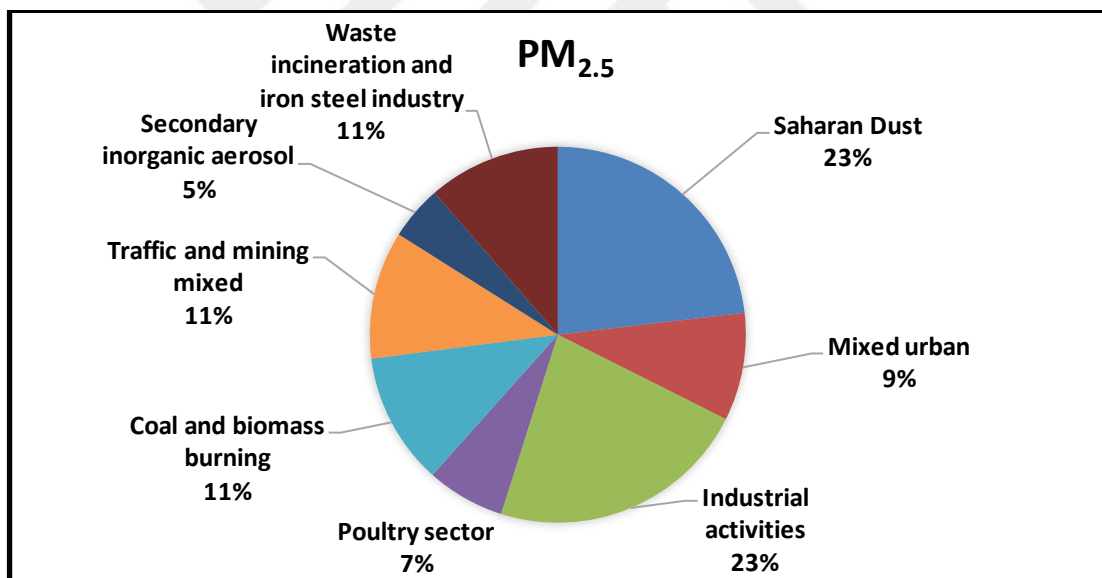


Figure 4.89. Percent contributions of each factor for $PM_{2.5}$

5. CONCLUSIONS AND RECOMMENDATIONS

With the growing technology and industrial activities, air pollution problem especially due to particulate matter pollution is an important issue for the environment and human health. Therefore, in this study we focused on determination of PM constituents and identification of the sources of PM.

The samples were collected in 3 different instruments. For the determination of inorganic species, a total of 326 PM_{2.5-10}, 312 PM_{2.5} samples and for the determination of EC/OC a total of 172 PM₁₀ and 166 PM_{2.5} samples were collected in the campus of Abant İzzet Baysal University between March 2013 and February 2014. Anions (Cl⁻, NO₃⁻, SO₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) and elements (Li, Be, Na, K, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hg, Ba, Hf, W, Pb, Bi, Tl, Th, U) were determined in samples. Concentrations of each parameter were evaluated statistically, temporally, and seasonally.

Elements, ions and EC-OC were analyzed by using ICP-MS, ion chromatography and OC-EC thermal optical analyzer, respectively. Method validation studies were done for each analysis. The results were also checked with SRM for element and ion analysis. Tungsten, Co, Se, Sb, V, NH₄⁺ and Mg²⁺ had higher percent errors (between -35% and 44%). OC-EC thermal optical analysis was checked with sucrose standard in every 10 analyses.

In PM_{2.5}, the most observed elements were Na, Mg, Al, Ca, Sc, Ti, Cr, Ce, Zn, Rb, Pb, Al, Ca, and Fe. In PM_{2.5-10}, the most observed elements were Ti, Th, Ca, Na, Mg, Al, Y, Nd. The most observed ions were Na⁺ and Cl⁻. OC concentrations were higher than EC concentrations. The average concentrations of Ca, Al, Fe, Mg, Na, K were higher than other elements in PM_{2.5} and PM_{2.5-10} during the whole sampling period. Data showed generally lognormal distribution. Amonium and Na⁺ in PM_{2.5-10}, Be and Na in PM_{2.5} showed normal distribution. EC in PM_{2.5-10} and Fe, Rb, Sb, Cs, Hg, NO₃⁻, NH₄⁺ and EC in PM_{2.5} showed Weibull distribution.

Generally, $PM_{2.5-10}$ concentrations were higher than $PM_{2.5}$ concentrations in whole year. The highest concentration was observed in May for $PM_{2.5}$ and in December for $PM_{2.5-10}$.

$PM_{2.5-10}/PM_{2.5}$ ratio was calculated for each parameters and the ratios were between 3.6 and 0.17. The elements Er, Sm, Y, Nd, Yb, Dy, Pr, Sr, Gd, Ho, Tb, Ce, La, Th, Ca, Fe, Eu, U, Lu, Be, EC, and OC were mostly observed in coarse fraction and As, Se, Zn, Pb, Cd, Sb, Sn, Cs, W, Hg, and Tl were mostly found in fine fraction.

Temporal variations of elements, ions and EC/OC were evaluated and crustal elements like Sc, Eu, Sm, Dy, Lu, Nd, U, Th, Er, Ho, Yb, Tm, Gd, Y and antropojenic elements like As and V showed similar trend in $PM_{2.5}$ and $PM_{10-2.5}$.

The concentrations of K^+ increased after August because of the increase in biomass burning. The arithmetic mean of NO_3^-/SO_4^{2-} ratio in $PM_{2.5}$ and $PM_{2.5-10}$ were 0.11 ± 0.13 and 0.38 ± 0.34 , respectively. The low values of ratio were a sign for high coal burning processes. There was a continuous source of NH_4^+ and NO_3^- because of the usage of fertilizer in the farming areas. There was an uncertainty in the source of SO_4^{2-} concentrations especially in May for $PM_{2.5}$. The SO_4^{2-}/K^+ ratios were higher in April and summer season because of the higher SO_4^{2-} concentrations in those days in $PM_{2.5}$. Back trajectories of days having high sulfate concentrations indicated the effect air mass flow coming from Black Sea. Seasonal variability of DMS-producing species in Black Sea might have affected the SO_4^{2-} concentrations.

The correlations of anion and cation were low in $PM_{2.5-10}$ and in $PM_{2.5}$. Neutralization of atmospheric particles was also evaluated and acidic particles were observed in the sampling site. Multiple linear regression was calculated to solve the acid base chemistry. Calcium ion was not involved in neutralization in $PM_{2.5}$. Because of the low correlation and uncertainty in acid base chemistry in PM, researcher should focus on ion chemistry of Bolu.

There is no significant difference between the concentrations of both EC and OC in different particulate size ranges. Two types of particles showed almost the same trend. The concentrations of OC_{sec} were generally larger than that of OC_{pri} . OC_{pri} concentrations were larger than OC_{sec} concentrations samples collected only in the

days of 04/09/2013, 05/09/2013, 23/09/2013, 28/09/2013, 9/10/2013, 7/11/2013, 26/11/2013, 2/12/2013, 7/12/2013.

The findings of the study were compared with similar areas in literature. Our results were higher than the rural areas and lower than the industrialized and urban areas. There were decline in the concentrations of Mg, Al, K, Ca, Cu, Zn, Cd, Sb, Pb, Bi in our study compared with previous two studies at the same sampling point. Mean concentration of La and As were similar in all three studies conducted at the same sampling point.

The source apportionment studies were also conducted by using crustal enrichment factor, wind sector analysis and PMF. The dominant wind sector was from the West South West sector in Bolu in whole sampling period. Pollution roses for each element and ions were also illustrated. Soil elements like Sr, Y, Er, Gd, Sm, were affected from the south direction. Antropogenic elements like As, Bi, Tl were mostly affected from the ESE wind sector which indicated the city center.

In the enrichment factor analysis, the EF values of Se, Sb, As, Cd, Hg, Pb, Cr, Sn, Mo, Zn, Ni, Ge, Sc, Ca, Cs, Ba, Mg, Al, Na in $PM_{2.5}$ and the EF values of Se, Sb, Hg, Cr, Cd, Mo, Zn, Sn, As, Pb, W, Ni, Cu, Sc, Ca, Ge, Ba in $PM_{2.5-10}$ had values higher than 10.

PMF version 5.0 was used in source identification studies for $PM_{2.5}$ and $PM_{2.5-10}$. The DISP error estimation studies and G space plots were used to support the estimation of source determination. The factors were supported by wind sector analysis and back trajectories.

For $PM_{2.5-10}$, eight factors were obtained. Tracer elements of the automobile gasoline, La and Ce, were observed in traffic factor. Arsenic, Bi, and Tl were explained in coal burning factor. Nitrate and SO_4^{2-} were also observed in $PM_{2.5-10}$ and this factor was called as aged particles contribution. Ammonium and K were a sign for biomass burning. Elements like Sr, Y, Rb, Pr, Nd, Sm, Dy, Er, Hf, Th, Co, Fe, Mn, V, Ca, Li were observed in the polluted soil factor and the soil factor in $PM_{2.5-10}$. Iron, La, Ce, Ba, Co and V were also observed in the polluted soil factor. Iron steel industry affected $PM_{2.5-10}$ and Sb, Cu, Fe, Ni, Zn were observed elements in the factor. $PM_{2.5-10}$ also

contained NH_4^+ , Cl^- , Na, Mg, Al, Ca, Sc, Fe, Cr and the back trajectories of the dates which had the highest G scores indicated the sea and long range transportation from Europe and Russia.

$\text{PM}_{2.5}$ were affected from eight factors in our study. Ammonium and K were observed in biomass and coal burning factor in $\text{PM}_{2.5}$. However, waste incinerator tracer Sb was observed in the same factor because people also burn their wastes in villages around the sampling area and in the incinerator in the cement factory. The crustal elements like Sr, Y, Pr, Nd, Sm, Dy, Er, and Yb were explained higher than 60% in Saharan dust factor. Ammonium was also observed in another factor with Cl^- because of high intensive poultry sector around the city. Particulate matters were also affected from the iron- steel industries coming from Karabük, Zonguldak. Industrial activities from Europe and Russia were also explained in another factor with Na, Mg, Al, Ca, Sc, Ti, Cr, Fe, Ba, Hg elements and Cl^- ion. Sulfate was explained highly in long range transportation factor and pollution roses were drawn with the highest G scores and it was indicated WSW direction. La and Ce, were also observed in traffic factor in $\text{PM}_{2.5}$. Antropogenic elements like NO_3^- , K, V, As, Se, Sn, Sb, Ba, W, Pb were observed in the long range transport from Europe-Russia and central Anatolia. The factors were supported by wind sector analysis and back trajectories. A summary of important elements for each factor in two types of particulate matter were summarized in Table 5.1 and 5.2.

Lantanium, Ce, and Pr were new tracers for vehicles emissions and the concentrations of the elements increased in each year. The researchers should also focus on these new tracers in future studies. Arsenic, Bi, Tl were found to be tracers for Turkish coal. These elements should always be determined to support the coal burning in the next studies.

Table 5.1. Summary of important elements for each factor in PM_{2.5}

Factor Name	Elements
Saharan dust factor	Sr, Y, Pr, Nd, Sm, Dy, Er, and Yb
Mixed urban contribution	NO ₃ ⁻ , K, V, As, Se, Sn, Sb, Ba, W, Pb
Industrial activities	Na, Mg, Al, Ca, Sc, Ti, Cr, Fe, Ba, Hg and Cl ⁻
Poultry sector	NH ₄ ⁺ and Cl ⁻
Coal and biomass burning	As, K, Tl, Pb, Hg, Sb, Sn, Mo and Bi
Traffic and mining mixed factor	La, Ce and Pr
Secondary inorganic aerosol	SO ₄ ²⁻
Waste incineration and iron steel factor	Fe, Co, Tl, Cd, Rb, As, Se, Sb, and K

Table 5.2. Summary of important elements for each factor in PM_{2.5-10}

Factor Name	Elements
Traffic Factor	La, Ce, Pr, Cd, Co, Ni, Cu, Cr, Mn, Mo, Sb, W, Hg, Pb
Coal burning	Tl, Bi, As, Cd, Sb, Pb, W, Hg, Cs
Aged particles	NO ₃ ⁻ , SO ₄ ²⁻
Biomass burning	NH ₄ ⁺ and K
Polluted soil factor	Sr, Y, Rb, Pr, Nd, Sm, Dy, Er, Ti, La, Ce, Eu, Gd, Yb, Hf, Th, U
Iron and steel industry	Sb, Cu, Fe, Ni, Zn
Soil factor	Mg, Al, K, Ca, Sc, V, Mn, Fe, Y, Rb, Pr, Nd, Sm, Dy, Er, Ti, La, Ce, Eu, Gd, Yb, Hf, Th, U
Sea and long range transportation	NH ₄ ⁺ , Cl ⁻ , Na, Mg, Al, Ca, Sc, Fe, Cr

PM_{2.5-10} concentrations were higher than PM_{2.5} concentrations in whole year. The highest concentration was observed in May for PM_{2.5} and in December for PM_{2.5-10}. Some samples had the higher PM concentration which determined by government, especially in winter season.

This study was focused on elemental, ionic and carbonaceous species in PM₁₀ and PM_{2.5}. In the literature, there were many studies about ultrafine PMs. In the future, studies about ultrafine PMs in the same sampling area will provide more information

about the sources. Furthermore, more comprehensive explanation of carbonaceous species (for examples determination of organic tracers) will also be helpful for the identifying of the pollutant sources.

In future works, active sampling of PMs in more than one sampling points can be achieved, the complete characterization of source profiles can be managed by using different receptor modeling approach.



6. REFERENCES

- Amin M, Lim LW and Takeuchi T (2008) “Determination of common inorganic anions and cations by non-suppressed ion chromatography with column switching”, *Journal of Chromatography A*, 1182 (2):169-175.
- Anonymous 1, www.mevzuat.gov.tr/Metin.Aspx?MevzuatKod=7.5.12188&MevzuatIliski=0&sourceXmlSearch=hava, accessed 19 May 2017.
- Anonymous 2, <http://www.nufusu.com/il/bolu-nufusu>, accessed 20 May 2017.
- Anonymous 3, www.google.com.tr/search?q=aib%C3%BC+kamp%C3%BCs+foto%C4%9Fraflar%C4%B1&source=lnms&tbm=isch&sa=X&ved=0ahUKEwjB-r2gs-XUAhURblAKHRuzDA8Q_AUIBigB&biw=1536&bih=714#tbm=isch&q=bolu+ili+hartas%C4%B1&imgsrc=pvqZbOHHBqvZ-:&spf=1498819712686, accessed 20 May 2017.
- Anonymous 4, www.ibu.edu.tr, accessed 20 May 2017.
- Anonymous 5, http://www.fenimining.com/upload/dosyalar/m_rapor_1359494018.pdf, accessed 20 May 2017.
- Arı A, Ertürk P and Gaga E (2015) “Yarı-kentsel bir bölgede toplanan PM_{2.5} örneklerinin kimyasal bileşiminin belirlenmesi”, *Proceeding Book of 6. Ulusal Hava Kirliliği ve Kontrolü Sempozyumu*, 826-839.
- Arimoto R, Duce, RA, Savoie DL, Prospero JM, Talbot R, Cullen JD, Tomza U., Lewis NF and Ray BJ (1996) “Relationships among aerosol constituents from Asia and the North Pacific during Pem-West A”, *Journal of Geophysical Research*, 101: 2011–2023.
- Baker A.R, Jickells TD, Witt M and Linge KM (2006) “Trends in the solubility of iron, aluminium, manganese and phosphorous in aerosol collected over the Atlantic Oceanic”, *Marine Chemistry*, 98: 43-58.
- Bäumer D, Vogel B, Versick S, Rinke R, Möhler O and Schnaiter M (2008) “Relationship of visibility, aerosol optical thickness and aerosol size distribution in an ageing air mass over South-West Germany”, *Atmospheric Environment*, 42: 989-998.
- Bolu Province Environmental Perspective Report (2010) T.C. Directorate of Environment and Urban Planning, Turkey.
- California ambient air quality standards (2005) Sacramento, CA, California Air Resources Board.
- Calvert JG and Stockwell WR (1984) SO₂, NO and NO₂ Oxidation mechanisms, *Atmospheric Considerations Butterworth, Boston*.

- Calvo AI, Alves C, Castro A, Pont V, Vicente AM and Fraile R (2013). “Research on aerosol sources and chemical composition: Past, current, and emerging issues”, *Atmospheric Research*, 120-121: 1-28.
- Castro LM, Pio CA, Harrison, RM, and Smith, DJT (1999) “Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations”, *Atmospheric Environment*, 33: 2771–2781.
- Central Pollution Control Board (2006) National ambient air quality standards, Delhi.
- Chang SY, Fang GC, Chou CCK and Chen WN (2006) “Source identifications of PM₁₀ aerosols depending on hourly measurements of soluble components characterization among different events in Taipei basin during spring season of 2004”, *Chemosphere*, 65:792-801.
- Charron A and Harrison RM (2005) “Fine (PM_{2.5}) and Coarse (PM_{2.5-10}) Particulate Matter on a Heavily Trafficked London Highway: Sources and Processes”, *Environmental Science and Technology*, 39:7768–7776.
- Cheung K, Daher N, Kam W, Shafer MM, Ning Z, Schauer JJ and Sioutas C (2011) “Spatial and temporal variation of chemical composition and mass closure of ambient coarse particulate matter (PM_{10-2.5}) in the Los Angeles area”, *Atmospheric Environment*, 45:2651-2662.
- Christian TJ, Yokelson, RJ, Cárdenas B, Molina LT, Engling G and Hsu SC (2010) “Trace gas and particle emissions from domestic and industrial biofuel use and garbage burning in central Mexico”, *Atmospheric Chemistry and Physics*, 10:565–584.
- Clements N, Eav J, Xie M, Hannigan MP, Miller SL, Navidi W., Peel JL, Schauer JJ, Shafer MM and Milford JB (2014) “Concentrations and source insights for trace elements in fine and coarse particulate matter”, *Atmospheric Environment*, 89: 373-381.
- Conselho Nacional do Meio Ambiente (2006) Brasília, Conselho Nacional do Meio Ambiente.
- Council Directive 1999/30/EC (1999) Relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. Official Journal L 163, 29/06/1999 page 41- 60.
- DeCarlo PF, Slowik JG, Worsnop DR, Davidovits P and Jimenez JL (2004) “Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 1: Theory”, *Aerosol Science and Technology*, 38:1185-1205.
- Dichotomus Air Sampler Instruction Manual (2015) Thermo Fisher Scientific Inc, USA.
- DPT (2002) Bolu İli Raporu.

- Draxler RR and Hess GD (1998) “An Overview of the HYSPLIT4 Modelling System for Trajectories, Dispersion, and Deposition”, *Australian Meteorological Magazine*, 47:295-308.
- EC (2004) Second Position Paper on Particulate Matter, European Commission.
- Echo PM User Manual (2004) TCR Tecora Srl Company, Italy.
- Einax JW, Zwanziger HW and Greiss S (1997) *Chemometrics in Environmental Analysis*, VCH, Wiley, New York.
- Environmental quality standards in Japan-air quality (2006) Ministry of the Environment, Tokyo.
- Finkelman RB and Peggy MKG (1999) “The types of data needed for assessing the environmental and human health impacts of coal”, *International Journal of Coal Geology*, 40.2:91-101.
- Gaga EO, Döğeroğlu T, Özden Ö, Ari A, Yay OD, Altuğ, H, Akyol, N, Örnektekin, S and Doorn WV (2012) “Evaluation of air quality by passive and active sampling in an urban city in Turkey: current status and spatial analysis of air pollution exposure”, *Environmental Science and Pollution Research*, 19:3579–3596.
- Garg BD, Cadle S H, Groblicki PJ, Mulawa PA, Laroo C and Parr GA (2000) *Brake-Wear Particulate Matter Emissions*, GM Research & Development Center Publication R&D 9033.
- Gildemeister AE, Hopke PK and Kim E (2007) “Sources of fine urban particulate matter in Detroit, MI”, *Chemosphere*, 69:1064-1074.
- Gray HA, Cass GR, Huntzicker JJ, Heyerdahl EK and Rau JA (1986) “Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles”, *Environmental Science and Technology*, 20:580–589.
- Harrison RM and Thorpe A (2008) “Sources and properties of non-exhaust particulate matter from road traffic: A review”, *Science of the total environment*, 400: 270-282.
- He K, Zhao Q, Duan YM, Yang FF, Shi Z and Chen G (2012) “Spatial and seasonal variability of PM_{2.5} acidity at two Chinese megacities: Insights into the formation of secondary inorganic aerosols”, *Atmospheric Chemistry and Physics*, 12: 1377–1395.
- Heinsohn, RJ and Kabel RL (1999) *Sources and Control of Air Pollution*, Prentice-Hall Inc., USA.
- Hildemann LM, Markowski GR and Cass GR (1991) “Chemical-composition of emissions from urban sources of fine organic aerosol”, *Environmental Science and Technology*, 25:744–59.

- Ho C, Chan C, Cho C, Lin H, Lee J and Wu C (2015) “Land used regression modelling with vertical distribution measurements for fine particulate matter and elements in an urban area”, *Atmospheric Environment*, 104:256-253.
- Hobbs P (2000) *Introduction to Atmospheric Chemistry*, Cambridge University Press, New York, USA.
- JRC reference Report, (2014) *European Guide on air pollution source apportionment with receptor models*. Report: EUR 26080 EN.
- IPCC (2007) *The Physical Science Basis*. In: *Contribution of Working Group I to the Fourth Assessment Report of the IPCC 2007* (ISBN: 978 0521 88009-1 Hardback; 978 0521 70596-7 Paperback).
- Kara M, Hopke PK, Dumanoglu Y, Altioek H, Elbir T, Odabasi M and Bayram A (2015) “Characterization of PM using multiple site data in a heavily industrialized region of Turkey”, *Aerosol and Air Quality Research*, 15:11-27.
- Karaca F, Nikov A and Alagha O (2006) “NN-AirPol: A neural-network-based method for air pollution evaluation and control”, *International Journal of Environmental Pollution*, 28, 3-4:310-325.
- Karakaş, D (1999) “Determination of the European contribution on the aerosol composition in the black sea basin and investigation of the transport mechanism”, METU Graduate School of Natural Applied Science, Ankara.
- Kasahara M (1992) *Chemical composition of atmospheric aerosol particles. Nucleation and atmospheric aerosols*. A. Deepak Publication.
- Koçak M, Mihalopoulos N and Kubilay N (2007) “Chemical composition of the fine and coarse fraction of aerosols in the northeastern Mediterranean”, *Atmospheric Environment*, 41:7351-7368.
- Paul K and Gadd J (2003) *Preliminary examination of trace elements in tyres, brake pads, and road bitumen in New Zealand*, Prepared for Ministry of Transport, New Zealand, Infrastructure Auckland.
- Kroll JH and Seinfeld JH (2008) “Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere”, *Atmospheric Environment*, 42:3593–3624.
- Legret M, and Pagotto C (1999) “Evaluation of pollutant loadings in the runoff waters from a major rural highway”, *Science of the Total Environment*, 235.1:143-150.
- Lim HJ and Turpin BJ (2002) “Origins of primary and secondary organic aerosol in Atlanta: Results of time-resolved measurements during the Atlanta supersite experiment”, *Environmental Science and Technology*, 36:4489–4496.
- Lin P, Hu M, Deng Z, Slanina J, Han S, Kondo Y, Takegawa N, Miyazaki Y, Zhao Y, and Sugimoto N (2009). “Seasonal and diurnal variations of organic carbon in

- PM_{2.5} in Beijing and the estimation of secondary organic carbon”, *Journal of Geophysical Research-Atmosphere*, 114, doi:10.1029/2008JD010902.
- Liu B, Song N, Dai Q, Mei R, Sui B, Bi X and Feng Y (2016) “Chemical composition and source apportionment of ambient PM_{2.5} during the non-heating period in Taian, China”, *Atmospheric Research*, 170:23-33.
- Madencilik Türkiye (2012) “Important developments from junior Nickel - Iron producer: Fe-Ni mining interview with Birol Kaya” *Mining Turkey*, 2:12- 15.
- Manahan SE (2000) *Environmental Chemistry*, Seventh Edition, CRC Press, USA.
- Martin F and Sjöberg K (2015) “Concentrations and emission factors for PM_{2.5} and PM₁₀ from road traffic in Sweden”, *Atmospheric Environment*, 119:211-219.
- McInnes LM, Quinn PK, Covert DS and Anderson TL (1996) “Gravimetric analysis, ionic composition, and associated water mass of the marine aerosol”, *Atmospheric Environment*, 6:869–884.
- Ministry of Health (2006) *Listado de normas oficiales mexicanas*, Mexico.
- NAAQS (2005) US Environmental Protection Agency, Washington, DC.
- Na K, Sawant AA, Song C and Cocker III DR (2004). “Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California”, *Atmospheric Environment*, 38: 1345–1355.
- National environment management: Air Quality Act (2004) Department of Environmental Affairs and Tourism, South Africa.
- Norris G and Brown S (2014) “EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide”, Washington, USA.
- Ott WR (1982). “Concepts of human exposure to air pollutants”, *Environment International*, 7:179–196.
- Öz M (2009) Characterization of PCBs, PAHs, and Organochlorine Pesticides in the Atmosphere of Bolu and Source Apportionment: Gas to Particle, Soil to Particle, Soil to Gas Exchanges, M.Sc. Thesis, Abant İzzet Baysal University Graduate School of Natural Applied Science, Bolu.
- Özlü E (2014) Source Apportionment of PM_{2.5}, PM_{2.5-10} and ozone in Bolu atmosphere in relation to meteorological variables, PHD Thesis, Abant İzzet Baysal University Graduate School of Natural Applied Science, Bolu.
- Paatero P and Hopke PK (2008) “Rotational tools for factor analytic models implemented by using the multilinear engine”, *Chemometrics*, 23 (2):91-100.

- Pacyna JM (1998) Source inventories for atmospheric trace metals, *Atmospheric particles: IUPAC Series on Analytical and Physical Chemistry of Environmental Systems*, vol. 5. Wiley, USA.
- Pandis SN, Harley RH, Cass GR and Seinfeld JH (1992). "Secondary organic aerosol formation and transport", *Atmospheric Environment*, 26A:2269-2282.
- Patnaik P (2010) *Handbook of environmental analysis: chemical pollutants in air, water, soil, and solid wastes*, CRC Press, USA.
- Perrone MG, Gualtieri M, Ferrero L, Lo Porto C, Udisti R, Bolzacchini E and Camatini M (2010). "Seasonal variations in chemical composition and in vitro biological effects of fine PM from Milan", *Chemosphere*, 78:1368-1377.
- Pio C, Cerqueira M, Harrison RM, Nunes T, Mirante F, Alves C, Oliveira C, Campa, AS, Artíñano B and Matos M (2011). "OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon", *Atmospheric Environment*, 45:6121-6132.
- Pope CAI, Ezzati M and Dockery DW (2009). "Fine-particulate air pollution and life expectancy in the United States", *New England Journal of Medicine*, 360:376-386.
- Sağırlı E (2013) *Chemical Composition of Particles at a Rural Site at Northwestern Turkey: Gateway to the Central Anatolian Plateau*, Ms. Thesis, Abant İzzet Baysal University Graduate School of Natural Applied Science, Bolu.
- Saydam AC, and Incigul P (1999) "The impact of saharan dust on the occurrence of algae blooms", *WIT Transactions on Ecology and the Environment*, 36.
- Saylor RD, Edgerton ES and Hartsell BE (2006). "Linear regression techniques for use in the EC tracer method of secondary organic aerosol estimation", *Atmospheric Environment*, 40:7546–7556.
- Schäfer K, Emeis S, Hoffmann H and Jahn C (2006). "Influence of mixing layer height upon air pollution in urban and sub-urban areas", *Meteorologische Zeitschrift*, 15:647-658.
- Schauer JJ, Rogge, WF, Hildemann LM, Mazurek MA, Cass GR and Simoneit BRT (1996). "Source apportionment of airborne particulate matter using organic compounds as tracers", *Atmospheric Environment*, 22:3837–3855.
- Schwarz J, Cusack M, Karban J, Chalupníčková E, Havránek V, Smolík J and Ždímal V (2016) "PM_{2.5} chemical composition at a rural background site in Central Europe, including correlation and air mass back trajectory analysis", *Atmospheric Research*, 176:108-120.
- Shen Z, Cao J, Arimoto R, Han Z, Zhang R, Han Y, Liu S, Okuda T, Nakao S and Tanaka S (2009). "Ionic composition of TSP and PM_{2.5} during dust storms and

- air pollution episodes at Xi'an, China”, *Atmospheric Environment*, 43 (18):2911–2918.
- Shridhar V, Khillare PS, Agarwal T and Ray S (2010) “Metallic species in ambient particulate matter at rural and urban locations of Delhi”, *Journal of Hazardous Material*, 175: 600–607.
- State Environmental Protection Administration (1996), *Ambient air quality standard National standards in People’s Republic of China*.
- Stein AF, Draxler RR, Rolph GD, Stunder BJB, Cohen MD and Ngan F (2015) “NOAA’s hysplit atmospheric transport and dispersion modeling system”, *American Meteorological Society*.
- Statgraph User Manual (2006) Statpoint Technologies inc, USA.
- Strader R, Lurmann F and Pandis SN (1999). “Evaluation of secondary organic aerosol formation in winter”, *Atmospheric Environment*, 33:4849–4863.
- Sun Y, Zhuang G, Wang Y, Han L, Guo J, Dan M, Zhang W, Wang Z and Hao Z (2004). “The air borne particulate pollution in Beijing- concentration, composition, distribution and sources”, *Atmospheric Environment*, 38:5991-6004.
- Sunset Laboratory Inc, (2013) *Organic Carbon / Elemental Carbon (OC/EC) Laboratory Instrument Manual*, USA.
- Torres A, Bond TC, Lehmann Suslick KS, Didenko Y, Fang MM, Hyeon T, Kolbeck KJ, McNamara WB, Mdeleleni M and Wong M (1999) *Philosophical Transactions of the Royal Society, London, Ser. A*:357-335.
- Tsai IT and Cheng MT (1999) “Visibility and aerosol chemical composition near the coastal area in Central Taiwan”, *Science of the Total Environment*, 231: 37-51.
- Turpin BJ and Huntzicker JJ (1995) “Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS”, *Atmospheric Environment*, 29:3527–3544.
- Turpin BJ, Saxena P and Andrews E (2000) “Measuring and simulating particulate organics in the atmosphere: problems and prospects”, *Atmospheric Environment*, 34: 2983–3013.
- Valavanidis A, Fiotakis K and Vlachogianni T (2008) “Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms”, *Journal of Environmental Science and Health Part C*, 26.4:339-362.
- Vallero D (2008) *Fundamentals of Air Pollution*, Fourth Edition, Elsevier Inc., USA.

- Wang Y, Zhuang G, Zhang X, Huang K, Xu C, Tang A, Chen J and An Z (2006) “The ion chemistry, seasonal cycle, and sources of PM_{2.5} and TSP aerosol in Shanghai”, *Atmospheric Environment*, 40:2935–2952.
- Watson JG, Chow J and Houck JE (2001) “PM_{2.5} source profile for vehicle exhaust, vegetative burning, geological material, and coal burning in Northwestern Colorado during 1995”, *Chemosphere*, 43:1141–1151.
- Westerlund KG, and Johansson C (2002) “Emission of metals and particulate matter due to wear of brake linings in Stockholm”, *WIT Transactions on Ecology and the Environment*, 53.
- WHO (2005) air quality guidelines, global update. Report on a Working Group meeting, Bonn, Germany, 18–20 October 2005.
- Yenisoy Karakaş S (2000) “Biomonitoring of the atmospheric pollutants at western Anatolia”, PHD Thesis, METU Graduate School of Natural Applied Science, Ankara.
- Yu S, Dennis RL, Bhawe PV and Eder BK (2004) “Primary and secondary organic aerosols over the United States: estimates on the basis of observed organic carbon (OC) and elemental carbon (EC), and air quality modeled primary OC/EC ratios”, *Atmospheric Environment*, 38:5257–5268.

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